Photochemistry of Chlorinated Biphenyls in Iso-octane Solution †

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The photolysis of a series of chlorinated biphenyls was examined in iso-octane at 254 nm. A triplet reactive state is implicated; it is concluded that the greater photolability of *ortho*-chlorinated biphenyls is due to their higher triplet energies. Excimers appear to play no role in the photodegradation. With triethylamine, fluorescent exciplexes are observed, and these may participate chemically in the decomposition of the least labile substrates.

THE ubiquitous occurrence of polychlorinated biphenyls (PCB) has prompted several investigations of their photochemistry.[1] Since these compounds are relatively unreactive both chemically and metabolically, it is argued that solar photodegradation may be important environmentally. The major photoreaction is stepwise replacement of chlorine by hydrogen, especially in solvents containing abstractable hydrogens.[2] In nucleophilic solvents such as methanol and water, substitution of the chlorine substituents also occurs to a small extent. All these reactions find precedent in the known photochemistry of other aryl halides.[3]

Previous work on PCB photochemistry has presupposed C–Cl photolytic cleavage in the primary

$$\mathrm{ArCl^*} \longrightarrow \mathrm{Ar\cdot} + \mathrm{Cl\cdot} \xrightarrow{\mathrm{RH}} \mathrm{ArH} + \mathrm{HCl} \qquad (1)$$

reaction (1). However, work in our laboratory[4] on other chloroaromatic compounds has shown that

$$\mathrm{X} + \mathrm{ArCl^*} \longrightarrow \mathrm{X^{\cdot +}} + \mathrm{ArCl^{\cdot -}} \longrightarrow \mathrm{Cl^-} + \mathrm{Ar\cdot} \xrightarrow{\mathrm{RH}} \mathrm{ArH} \qquad (2)$$

electron transfer processes may be important [equation (2)], in the case of 1-chloronaphthalene to enhance photoreactivity, for chlorobenzene to depress it. The work of Ohashi *et al.*[5] on 4-chlorobiphenyl suggests the possible importance of electron transfer in the PCB series also.

The aims of our investigation were (i) to assess the role of excimers and exciplexes in PCB photochemistry, and (ii) in view of the recent finding of greater mutagenicity of less rather than more heavily chlorinated PCB,[6] to study compounds of varying levels of chlorination. In this paper we report the results of our studies of the mechanism in a hydrocarbon solvent, iso-octane.

At the outset of this work, it was decided to examine the mechanism of the reaction following excitation of the substrates at 254 nm, rather than the environmentally more significant 300 nm. The reason is a practical one.

The first $^1\pi,\pi^*$ transition of biphenyl occurs near 247 nm (ε 18 000).[7] *ortho*-Substitution shifts this transition to shorter wavelength and decreases its intensity; this is because of the loss of conjugation that occurs due to twisting about the inter-ring bond. At 300 nm only the tail of the absorption band is being excited; at comparable concentrations the absorbance of an *ortho*-

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chlorinated PCB is very much less than that of one lacking *ortho*-substituents. Consequently, photolysis affords a dechlorination product having a much greater extinction coefficient at 300 nm, for Ruzo *et al.*[2a] had noted the preferential loss of *ortho*-chlorines. After a small conversion, much of the light is absorbed by product(s). It is very difficult to photolyse to conversions so small that the products do not absorb substantially, and quantum yields of reaction therefore tend to be badly underestimated. An example of this behaviour is shown by 2,3,5,6-tetrachlorobiphenyl which after <10% conversion afforded equal amounts of 2,3,5-trichlorobiphenyl and the secondary product 3,5-dichlorobiphenyl.[8] The same problems pertain in principle at 254 as at 300 nm, but they are not as serious in practice.

Role of Excimers.—The fluorescence of concentrated solutions of biphenyl, 4-chlorobiphenyl, and 2,2′,5,5′-tetrachlorobiphenyl gave no indication of excimer emission. The shape of the emission curve was distorted due to self absorption at the high energy end, but was independent of temperature. Apparent enthalpies of association were typically -1.2 ± 0.4 kJ mol^{-1} * (contrast 1-chloronaphthalene[9] -11 ± 1 kJ mol^{-1}). In addition, the quantum efficiencies of photoreaction of 4-chloro- and 2,2′,5,5′-tetrachloro-biphenyl were independent of concentration over the range 10^{-2}—10^{-4}M. Again, this contrasts with what was observed previously for 1-chloronaphthalene and chlorobenzene.[4] We conclude that excimers play no important role in the direct photolysis of PCB which thus proceeds by the homolysis mechanism [equation (1)] rather than through the excimer [equation (2; X = ArCl)].

Why should PCB behave differently from these other aryl halides? We advance two suggestions. (i) The biphenyl nucleus is rod like, in contrast to the disc-like shapes of arenes that usually give excimers. Fewer favourable associative configurations of the dimer exist (ii) Biphenyls are nonplanar in solution, even without the complication of *ortho*-substitution.[7] Excimer formation requires the two aromatic nuclei to lie parallel;[10] energy is needed to achieve planarity. Since the enthalpies of association are usually small, the steric strain in the hypothetical PCB excimer very probably exceeds the stabilization to be gained from association.

Quantum Yields.—Quantum yields for various photoprocesses of the PCB we have studied are given in Table 1. Quantum yields of fluorescence were obtained by relative intensity, and are calibrated against the known quantum yield of fluorescence of biphenyl.[11] The literature values of Dreeskamp *et al.*[12] in EPA at 77 K are given for comparison with ours, which were obtained in aerated solutions of iso-octane at 23 °C. We note that the fluorescence quantum yields are not strongly temperature dependent;[13] almost all † are <0.1.

TABLE 1

Photoprocesses of chlorinated biphenyls[a]

Substituents	ϕ_F	Lit. value[b]	ϕ_P[b]	ϕ_r[c] (lit.)
None	0.2[d]	(0.17)	0.25	
2[e]	0.09	(<0.02)	0.46	0.39 ± 0.02
3	0.07	(0.08)	0.27	0.0011 ± 0.0002
4	0.07	(0.04)	0.60	0.0006 ± 0.0001
2,4	0.02			0.62 ± 0.05
2,5	0.06			0.13 ± 0.01
2,2′	0.005	(<0.01)	0.95	0.16 ± 0.01
4,4′	0.59	(0.04)	0.63	0.0006 ± 0.0001
2,4,5	0.11			0.43 ± 0.08 (0.05)[f]
2,4,6	0.003			0.14 ± 0.02 (0.02)[f]
2,2′,4,4′	0.02	(<0.01)	0.94	0.45 ± 0.01 (0.10)[g]
2,2′,5,5′	0.007			0.0053 ± 0.0004 (0.01)[g]
3,3′,4,4′	0.08			(0.005)[g]
3,3′,5,5′	0.02	(0.01)	0.41	0.0003 ± 0.0001 (0.002)[g]
2,2′,4,4′,6,6′	0.003		1.0	

[a] 1.0×10^{-3}M solutions in iso-octane, 23 °C, excitation 290—310 nm, aerated solutions. [b] Ref. 12, in EPA at 77 K. [c] Photolysis at ambient temperature, 254 nm. [d] Ref. 11. [e] Fluorescence data may be unreliable as *ca.* 1% of biphenyl was present. [f] Ref. 8 at 300 nm. [g] Ref. 2*a*, at 300 nm.

The low quantum yields of fluorescence, especially of the highly chlorinated PCBs, are compatible with the relatively high quantum yields of phosphorescence reported by Dreeskamp *et al.*[12] at 77 K, and therefore also with high quantum yields of intersystem crossing at 77 K. Ruzo *et al.*[2a] reported that intersystem crossing occurred with unit efficiency at room temperature; although fluorescence is incompatible with a unit intersystem crossing efficiency, it is likely that most photoexcited PCB molecules pass into the triplet state, especially if several *ortho*-chlorines are present.

Quantum yields of reaction (at 254 nm) cover a much greater range than those reported.[2a,8] As found previously,[2a] *ortho*-substitution greatly enhances photoreactivity, and the following trends seem to be apparent. (i) *para*-Chlorination increases the efficiency of cleavage of an *ortho*-chlorine: compare 2,4-dichloro- with 2-chloro-biphenyl, and 2,2′,4,4′-tetrachloro- with 2,2′-dichloro-biphenyl. (ii) *meta*-Chlorines decrease photoreactivity: compare 2-chloro- with 2,5-dichlorobiphenyl, 2,4-dichloro- with 2,4,5-trichloro-biphenyl, and 2,2′-dichloro- with 2,2′,5,5′-tetrachloro-biphenyl. (iii) One *ortho*-chlorine promotes the greatest photodecomposition efficiency: compare 2-chloro- with 2,2′-dichloro- and 2,4,6-trichloro-biphenyl. Such an effect has been ob-

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* Results obtained were biphenyl, ΔH -1.4 ± 0.4, -4 ± 1; 4-chlorobiphenyl, -3.0 ± 0.4, 4,4′-dichlorobiphenyl, -1.0 ± 0.7 kJ mol^{-1}.

† We have no explanation of the anomalously high ϕ_F in the case of 4,4-dichlorobiphenyl.

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[9] Y. Kumar, unpublished work.

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[12] H. Dreeskamp, O. Hutzinger, and M. Zander, *Z. Naturforsch.*, 1972, **27a**, 756.

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served previously for bromobiphenyls;[14] its explanation is that fission of the *last ortho*-chlorine allows the greatest relief of steric strain in the excited state.

Assignment of Excited State.—It was shown above that heavily chlorinated PCBs pass into the triplet state with high efficiency upon photoexcitation. For a compound such as 2,2′,4,4′-tetrachlorobiphenyl, a quantum yield of reaction of 0.45 can be compatible only with a triplet reactive state if ϕ_{isc} is *ca.* 1.[2a] Energetically, this may seem inconsistent with a C–Cl bond dissociation energy of the order of 330 kJ mol^{-1} [15] and a triplet excitation energy of 270 kJ mol^{-1} [16] in the biphenyl series. The answer may be found in the shift to higher energy[12,16] of the phosphorescence of orthosubstituted biphenyls. The spectra of Dreeskamp *et al.* suggest a high energy cut off of phosphorescence of *ca.* 270 for 4,4′-dichlorobiphenyl, and *ca.* 300 kJ mol^{-1} for the 2,2′,4,4′-tetrachloro compound. Additionally, Wagner[17] has concluded that, at least for the parent biphenyl system, the 0–0 band is not observed spectroscopically. It lies at higher energy than the onset of phosphorescence.

Arguments about photon balance cannot be applied to the less reactive compounds. Not only is ϕ_r much reduced, but in a case such as 4-chlorobiphenyl, ϕ_{isc} may be lower too.

Conventional sensitisation and quenching studies are difficult to apply in the biphenyl series. The relatively high triplet energy suggests the use of ketone sensitisers, yet Wagner and Scheve[16b] have found energy transfer from benzophenone to *ortho*-substituted biphenyls to be very inefficient. We attempted to sensitise the photolysis of two representative chlorobiphenyls. In the case of 2-chlorobiphenyl, sensitisation did occur, but with an efficiency of only 0.1%. Correspondingly, Wagner and Scheve found that 2-chlorobiphenyl quenched the phosphorescence and the photoreduction of benzophenone much less efficiently than did biphenyl itself. An attempt to sensitise the photodecomposition of 4-chlorobiphenyl was unsuccessful. 4-Chlorobiphenyl is photolysed so inefficiently that all that could be observed were benzophenone photoreduction products. Moreover, small amounts of benzophenone quenched the fluorescence of 4-chlorobiphenyl, raising the possibility that electron transfer processes may be important in this system.

In the same way, diene quenching of the reaction cannot be interpreted simply as suppression of a triplet state reaction. As seen in Table 2, cyclohexa-1,3-diene quenches the fluorescence of PCB, in addition to any effect it may have on the triplet state. Shetlar[18] has demonstrated that it is very difficult to draw confident mechanistic conclusions in cases where two states are simultaneously quenched. Ruzo *et al.*[2a] used cyclohexadiene quenching of PCB photodecomposition to estimate triplet lifetimes in solution. Their results must be viewed with reserve since singlet quenching also occurs.

Recently, Morrison *et al.*[19] have used xenon to elucidate the multiplicity of photoreactions; the heavy atom promotes the conversion $S_1 \longrightarrow T_1$. The less chlorinated PCB are believed to have relatively small ϕ_{isc}; thus their efficiency of photodecomposition should be enhanced in the presence of xenon if the triplet is reactive, but reduced if a reactive singlet state is involved. PCB having high ϕ_{isc} should be indifferent to the presence of xenon.[20]

TABLE 2

Fluorescence quenching data for chlorinated biphenyls in iso-octane[a]

	$k_q\tau$/l mol^{-1}			
Substituents	Et_3N($\lambda_{\text{exc.}}$ nm)[b]	C_6H_8[c]	CH_3I	C_3H_7Br[d]
None	79 (440)	1 800	350	1.4
2[e]	54	120		
3	17 (420)			
4	26 (430)	490	100	
2,5	3			
4,4′	15 (450)	45		0.3
2,4,5	3			
2,4,6	7 (450)	290	25	0.5
2,2′,4,4′	0.2		28	
2,2′,5,5′	6 (430)	180	31	
3,3′,4,4′	17 (445)			
3,3′,5,5′	16 (465)	35		

[a] PCB concentration 1.0 × 10^{-3}M, aerated solutions, 23 °C. [b] $\lambda_{\text{max.}}$ for triethylamine exciplex emission. [c] Cyclohexa-1,3-diene. [d] 1-Bromopropane. [e] The relatively ready quenching of fluorescence may be due to the biphenyl impurity (1%).

The xenon assisted reaction was studied for four chlorobiphenyls (Table 3). Heavy atom quenching was first demonstrated using methyl iodide as quencher (Table 2). Ampoules of PCB in iso-octane with and without xenon (*ca.* 1 atm.) were irradiated in parallel, following measurement of the fluorescence intensity of each ampoule. Both xenon and methyl iodide were more efficient at quenching the fluorescence of 4-chlorobiphenyl than that of more highly chlorinated analogues.

TABLE 3

Effect of xenon on photodecomposition of PCB

	I_F[a]				% Decomposed[b]	
Substituents	No Xe	Xe	Photon flux (quanta s^{-1})	Irradiation time (h)	No Xe	Xe
4	28	25	5.0 × 10^{16}	11	26	37
2,4,6	17	16	1.2 × 10^{16}	0.167	43	47
2,2′,4,4′	15	14	1.2 × 10^{16}	0.083	25	25
2,2′,5,5′	30	29	5.0 × 10^{16}	0.50	16	18

[a] Fluorescence intensity, arbitrary units. [b] Initial PCB concentration was 5 × 10^{-3}M.

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[14] N. J. Bunce, S. Safe, and L. O. Ruzo, *J.C.S. Perkin I*, 1975, 1607.

[15] S. W. Benson, 'The Foundations of Chemical Kinetics,' McGraw-Hill, New York, 1960, p. 670.

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[19] H. Morrison, T. Nylund, and F. Palensky, *J.C.S. Chem. Comm.*, 1976, 4.

[20] Despite our success with this technique reservations have been expressed about it, J. B. Birks, *Photochem. Photobiol.*, 1976, **24**, 287.

The photodegradation of 4-chlorobiphenyl was enhanced in the presence of xenon; this is consistent with a triplet state photoreaction, where xenon increases the stock of triplets by its effect on $S_1 \longrightarrow T_1$ intersystem crossing. If 4-chlorobiphenyl had reacted from the higher energy singlet, the opposite effect on photoreactivity would have been expected. The efficiencies of reaction of the more reactive compounds 2,4,6-trichloro-, 2,2′,5,5′-tetrachloro-, and 2,2′,4,4′-tetrachlorobiphenyls were almost unaffected by xenon. This is reasonable if $S_1 \longrightarrow T_1$ intersystem crossing is already very efficient.*

We conclude that reaction occurs predominantly from the triplet excited state of both the reactive and the unreactive groups of PCB compounds. The striking difference in quantum yield between compounds with and without *ortho*-chlorine substituents may be attributed to the higher triplet energies of the former group. When one *ortho*-methyl (and presumably also chloro) substituent is present, the triplet remains planar,[17b] and the higher energy is associated with non-bonded interactions. When methyl groups are present in the 2,2′-positions, two conformers result; the triplet of one (*E*) is planar, while the other (*Z*) is twisted.[23] Extrapolation suggests that PCB having three or four *ortho*-chlorines would have twisted triplets. One point that remains unclear concerns the energetics of the C–Cl bond homolysis. For a compound such as 4-chlorobiphenyl, with no steric strain due to *ortho*-chlorines, the homolysis appears to be very endothermic. Further work will be needed to understand this point.

Amine-assisted Photolysis.—Ohashi *et al.* reported that, in acetonitrile, 4-chlorobiphenyl is photodegraded by way of an exciplex in the presence of the donor triethylamine.[5] In iso-octane the situation is similar, and a fluorescent exciplex is observed for 4-chlorobiphenyl and for other PCB species (Table 2). We measured the quenching constants for quenching the fluorescence of several PCBs with triethylamine; we also studied qualitatively the effect of triethylamine on the decomposition efficiency (Table 4).

Those compounds whose photolysis proceeds readily in the absence of triethylamine (*i.e. ortho*-substituted PCB) are quenched much less efficiently, and the amine has much less effect on the ease of decomposition. We argued above that intersystem crossing is probably more efficient for *ortho*-chlorinated biphenyls, so that the ability of triethylamine to interact with the singlet would be impaired. Reaction from a singlet exciplex would therefore be unlikely for an *ortho*-chlorobiphenyl. However, for a light stable substance such as 3- or 4-chlorobiphenyl, exciplex formation provides a new route for photodegradation.

TABLE 4

Effect of triethylamine on PCB photoreactivity [a]

Substituents	Photon flux (photon s^{-1})	Irradiation time (h)	Amount used (%)	
			No Et_3N	Et_3N present
3	4.3×10^{16}	24	42	98
4	4.3×10^{16}	24	16	100
4,4′	4.3×10^{16}	24	16	100
2,4	9.0×10^{15}	0.033	14	18
2,4,6	4.3×10^{16}	0.083	40	52
2,2′,4,4′	9.0×10^{15}	0.041	14	16
2,2′,5,5′	4.3×10^{16}	6	42	80

[a] Initial PCB concentration 5×10^{-3}M; Et_3N concentration 5×10^{-2}M.

EXPERIMENTAL

Chlorinated biphenyls were obtained commercially or synthesized by the method of Cadogan.[24] They were purified by preparative t.l.c. and their purities checked by g.l.c. Physical properties have been described elsewhere.[25] 2-Chlorobiphenyl was purified by preparative g.l.c. (SE 30 at 180°); it contained *ca.* 1—2% of biphenyl as an impurity.

Iso-octane was commercial material, purified by reflux over fuming H_2SO_4. It was washed with water, dried ($CaCl_2$), and fractionally distilled, b.p. 99 °C. Its purity was checked by absorption and fluorescence spectroscopy.

Fluorescence spectra were recorded at room temperature in 1 cm × 1 cm square quartz cuvettes using a Hitachi–Perkin-Elmer model MPF 2A. For low temperature work and for degassed samples, a Farrand Mark I fluorometer was employed. Sample chambers for these applications were designed and constructed in this department.

Fluorescence quantum yields were determined at 23 °C relative to biphenyl. A 1.0×10^{-3}M solution of the biphenyl was excited (λ usually 280—310 nm) and its fluorescence intensity (λ 320—340 nm) measured. The response of the photomultiplier was assumed constant over this wavelength range. The ratios of intensities were taken to be ratios of fluorescence quantum yields.

Fluorescence quenching constants were determined by the Stern–Volmer method. Seven solutions were used for each run. Stock solutions (1×10^{-2}M of the PCB) and an appropriate concentration of quencher stock solution were made. Into each of seven 10 ml volumetric flasks were pipetted 1 ml of PCB stock solution and 0.0, 0.0, 0.5, 1.0, 2.0, 3.0, and 5.0 ml of quencher stock solution. All were diluted to 10 ml with iso-octane.

Fluorescence quenching by benzophenone was studied for 4-chlorobiphenyl. The 4-chlorobiphenyl concentration

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* A rather different kind of heavy atom effect has been observed in the depression of aryl halide photoreactivity by halide ions.[21] For a variety of aryl halides, including some PCB, the photolysis efficiency was unaffected by adding chloride ion, but depressed by bromine and iodide. Curiously, bromide was also as effective as iodide. This is not a typical heavy atom effect; for example, in our fluorescence quenching studies, $k_q\tau$ values for biphenyl and 2,4,6-trichlorobiphenyl were 1.4 and 0.5 l mol^{-1} when 1-bromopropane was the quencher, but 350 and 25 l mol^{-1} with methyl iodide. In a study of quenching of biphenyl fluorescence by inorganic ions, Watkins [22] concluded that charge transfer contributed significantly to the quenching mechanism. Quenching constants for Cl^-, Br^-, and I^- were in the ratio 1 : 7 : 17. Although reactions examined by Ruzo *et al.*[21] proceed from triplet states, it is possible that the $T_1 \to S_0$ intersystem crossing is also assisted by electron transfer. This could explain why bromide and iodide are similarly effective in quenching the reaction, but chloride has no effect, due to the greater electron affinity of chlorine.

[21] L. O. Ruzo, G. Sundstrom, O. Hutzinger, and S. Safe, *Rec. Trav. chim.*, 1977, **96**, 249.

[22] A. R. Watkins, *J. Phys. Chem.*, 1973, **77**, 1207.

[23] B. J. Scheve and P. J. Wagner, *Chem. Phys. Letters*, 1974, **25**, 324.

[24] J. I. G. Cadogan, *J. Chem. Soc.*, 1962, 4257.

[25] O. Hutzinger, S. Safe, and V. Zitko, *Bull. Environ. Contam. Toxicol.*, 1971, **6**, 209.

was 5×10^{-3}M, while that of benzophenone ranged up to 3×10^{-3}M. Raw fluorescence intensities were corrected for light absorption by benzophenone at the excitation wavelength (295 nm). A Stern–Volmer plot of the corrected intensities gave $k_q\tau$ as 100 l mol^{-1}.

Samples for photolysis were degassed by the freeze–pump–thaw method (usually two cycles at 0.02 mm). Photolyses were carried out in duplicate, using quartz ampoules of 8 mm o.d., fused by graded seals to Pyrex tubing for evacuation. Sample size was normally 2.0 ml. The photolysis equipment was a Rayonet model RPR photoreactor equipped with 16 low pressure mercury lamps with emission mainly at 254 nm. A ' merry-go-round ' was used to ensure equal illumination of the samples. Photolysed samples were analysed for substrate disappearance by g.l.c. using a Carle model 9500 gas chromatograph equipped with flame ionization detector and 6 ft × 1/8 in stainless steel columns of 10% SF96 on Chromosorb W. All samples were analysed at least in duplicate using the internal standard method. Only alkanes were chosen as internal standards to avoid interference with photoreactivity. Actinometry was by the method of Hatchard and Parker [26] using potassium ferrioxalate. For the more reactive PCB, fewer than the full complement of sixteen lamps was used. The data recorded in Table 1 represent the average of at least four samples; more often, up to a dozen samples were used, and the conversion of reactant demonstrated to be linear with time. This shows that light absorption by products is unimportant at the conversions used.

Xenon for quenching studies was Matheson Research Grade material. A small portion of the vacuum system was evacuated and filled with xenon to a pressure of 5 lb in^{-2}. This was condensed into the ampoules, whose volumes were adjusted so that they were approximately one third the volume of the volume containing xenon. Thus the final xenon pressure above the samples was approximately one atmosphere, and the PCB concentration was 5.0×10^{-3}M. After sealing, these ampoules, together with appropriate controls, were examined by fluorescence spectroscopy before photolysis. The results are in Table 3.

The photolysis of 2-chlorobiphenyl was sensitised by benzophenone. The solutions (2.0 ml) contained 2-chlorobiphenyl (5.0×10^{-3}M) with or without sensitiser (8.0×10^{-3}M). In the sensitised reactions, the sensitiser absorbed 85% of the light. After 180 s photolysis at 254 nm the sensitised solutions had reacted to the extent of 4%, the unsensitised ones 16%. Thus after correcting for 15% direct reaction, the rate of the sensitised reaction was 4.4×10^{-7} mol l^{-1} s^{1}. From the photon flux (1.9×10^{-8} einstein s^{-1}) and the known [27] lifetime of triplet benzophenone, the steady state concentration of benzophenone triplets was 2.0×10^{-11}M. Then the rate of energy transfer is given by $k_t[^3Ph_2CO][C_{12}H_9Cl]$ which is also the rate of the sensitised reaction/ϕ_r. From this, we calculate k_t as 1.1×10^7 l mol^{-1} s^{-1}. This is higher than Wagner and Scheve's value,[16b] but 10^3 lower than the rate of diffusion.

The effect of concentration was studied over the range 10^{-2}—10^{-4}M for decomposition of two PCB isomers at room temperature. The results are in Table 5.

TABLE 5

Effect of concentration on PCB photoreactivity [a]

	10^{-4} Decomposition (l mol^{-1} h^{-1})		
	10^{-2}M	10^{-3}M	10^{-4}M
4-Cl	1.8	1.3	1.5
	1.6	1.1	1.5
2,2′,5,5′	3.4	2.7	2.8

[a] Initial concentration 5×10^{-3}M. Conversion of 4-Cl was *ca.* 20%, of 2,2′,5,5′-Cl_4 *ca.* 70%.

For the reactions in the presence of triethylamine, the initial PCB concentration was 5.0×10^{-3}M and that of triethylamine 5.0×10^{-2}M. Irradiation times and photon fluxes varied so as to give convenient amounts of decomposition. The results are in Table 4.

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