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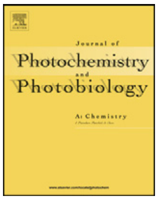

Wavelength dependence of luminescence and quantum yield in dechlorination of PCBs

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ABSTRACT

Direct photolysis of many PCBs has a non quenchable component which survives oxygen quenching. In this study, the nature of the excited states of PCB 138 and PCB 77 was analyzed to understand the origins of reaction from singlet as well as triplet excited states. Data on luminescence quenching, luminescence profiles, reaction quantum yields, and product distributions as functions of excitation wavelength were collected. The most striking and unambiguous observation was the excitation wavelength dependence of the vibronic structure of a fluorescence. Dependence of the apparent quantum yields on the reaction conditions (concentration, intensity) was also recognized during this study. Upon correlating all collected data, sufficient evidence for slow vibrational relaxation in a 2,2′-dichloro congener emerged. This could be seen to open opportunities for reaction from the singlet in competition with intersystem crossing. The slow vibrational relaxation can be understood through analogy to quantitatively modeled biphenyl spectra, to arise from steric hindrance and solvent resistance to rotation about the central C–C bond.

1. Introduction

Substantial research on the dechlorination of polychlorinated biphenyls (PCBs) using light has been conducted over a number of years, yet some mechanistic issues remain. The recognition of a promising photochemical chain reaction in basic 2-propanol by Hawari et al. [1] and the description of a pilot system for its application to remediation of PCBs in soils by Jakher et al. [2] renew interest in the mechanisms.

It is generally suggested that the first excited triplet state of a PCB, which is produced in good yield, is the main precursor of dechlorination. Often this state is taken to be primarily responsible for the reactivity of PCBs. Nonetheless, there is some strong evidence that a singlet excited state might be involved in the dechlorination of PCBs. This paper provides further clarification of the role of the several excited states.

In the past, researchers have used three approaches to determine the multiplicity of the reactive excited state: quenching by biacetyl and dienes, xenon assisted reactions and benzophenone sensitization methods. Ruzo et al. [3] studied six symmetrical tetrachlorobiphenyls in cyclohexane and methanol under 300 nm irradiation using 3-cyclohexadiene as the triplet quencher. They reported the quantum yield of the inter-system crossing (ISC) to be ~1.0, thus they concluded that the photochemistry arose exclusively from the triplet. However, Bunce et al. [4] identified two problems with using a diene quencher: first, fluorescence can be quenched along with the triplet and second, a diene can act as an inner filter and results should be corrected. To clarify the multiplicity issues, Bunce et al. [4] studied xenon assisted reaction of a series of chlorinated biphenyls in isooctane using 254 nm lamps. They concluded that reaction predominately occurs through the triplet state of both more reactive (ortho-chloro biphenyls) and less reactive (non-ortho) PCB congeners. Nordblom and Miller reported inefficient biacetyl quenching of the excited state of 4,4′-dichlorobiphenyl in 2-propanol irradiated at 310 nm [5]. Assuming diffusion controlled quenching they calculated an excited state lifetime of only 10^{-6} s for a triplet excited state, which they argued is probably too short. Hence the nature of the reactive excited state remained unresolved in their paper. However, Ruzo and Bunce [6] recommend caution in the interpretation of triplet lifetimes obtained by the quenching methods for two main reasons: first, anomalous quenching of the triplet excited state of some aryl halides has been observed and secondly, quenching might not be diffusion controlled. These authors assign the triplet excited state as the reactive excited state in the photoreaction.

Involvement of a singlet excited state for some PCBs was reported by Nishiwaki et al. [7,8]. Their results are based on quenching reaction with 1,3-cyclohexadiene, 1,3-pentadiene or biacetyl, fluorescence quenching data, and photosensitized dechlorination using acetone and acetophenone. Their results indicate that the

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singlet excited state is the only reactive excited state for 2-, and 3-chlorobiphenyl and singlet along with triplet excited states is involved in photodechlorination of 3,4-dichlorobiphenyl. Nishiwaki et al. reported on mono and di-chlorobiphenyls, but our oxygen quenching results [7] for PCB 138 (a hexachlorobiphenyl) in alkaline 2-propanol under 254 nm excitation suggested a non-quenchable component in the reaction that survives oxygen quenching, even though fluorescence can be partially quenched by oxygen. Bunce et al. [4] have also commented briefly that their efforts at determining the nature of the excited state using oxygen quenching were inconclusive because oxygen did not act as a quencher [9]. They did not include experimental evidence for this intriguing observation. This is presumably because of a reaction path from the PCB singlet involving the higher excited state in the photochemistry. Higher excited state photochemistry can be observed when radiationless deactivation rates are unusually slow or when radiative or photochemical rates are fast compared to internal conversion or intersystem crossing. To understand this, it is necessary to discover the factors that govern competition among pathways in the short time domain. Four processes may compete in the picoseconds or even sub-picoseconds domains: (1) vibrational relaxation, (2) internal conversion, (3) intersystem crossing, and (4) the initial step on the photoreaction path. The simplest approach is to look for measurable variations of photochemical and photophysical yields over appropriate frequency domains [10,11].

Measurement of the quantum yields of the reaction in comparison to the relative fluorescence yields at different wavelengths was the approach initially taken for this study rather than quenching studies and sensitization approaches. If fluorescence yield is wavelength dependent, upper excited states will have pathways distinct from crossing to lower ones. It is known that many reactions, from short lived excited states, display wavelength dependent quantum yield, even across a single electronic band [10]. Preliminary results yielded different intensities of fluorescence at different wavelengths of excitation under conditions designed to produce intensities that map yields. However, variations were greater than expected, suggesting that conditions were not as well controlled as needed. Therefore it was decided to compare the shape of the fluorescence spectrum envelope at different wavelengths of excitation. In parallel, apparent quantum yields of dechlorination reaction at different wavelengths in 2-propanol were measured as well as dependence of photolysis intermediate distribution as a function of wavelength. The quantum yields are labelled “apparent” because the yields depended upon both light intensity and concentration. A review of the wide variety of quantum yields reported in literature supports the idea that quantum yields depend on both PCB concentration and light intensity [1–5].

2. Materials and methods

2.1. Materials

Standards of PCB congeners used in this study, 2,4′-dichlorobiphenyl (PCB 8); 4,4′-dichlorobiphenyl (PCB 15); 2,4,4′-trichlorobiphenyl (PCB 28); 3,4,4′-trichlorobiphenyl (PCB 37); 2,2′,5,5′-tetrachlorobiphenyls (PCB 52); 2,3′,4,4′-tetrachlorobiphenyl (PCB 66); 3,3′,4,4′-tetrachlorobiphenyl (PCB 77); 2,2′,3′,4,5-pentachlorobiphenyl (PCB 97); 2,3,3′,4,4′-pentachlorobiphenyl (PCB 105); 2,3′,4,4′,5-pentachlorobiphenyl (PCB 118); 2,2′,3,4,4′,5′-hexachlorobiphenyl (PCB 138); 2,2′,4,4′,5,5′-hexachlorobiphenyl (PCB 153) were obtained from Chromatographic Specialties Inc. 2-Propanol (HPLC grade) was used as purchased from Sigma–Aldrich. Distilled deionized water was used whenever required in the experiments.

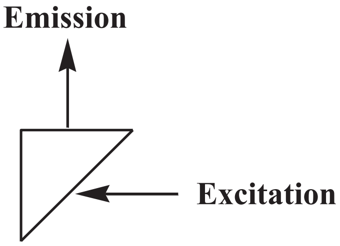

Fig. 1. The geometry of the triangular cell in the spectrofluorometer.

2.2. Methods

2.2.1. Fluorescence measurements

Fluorometric measurements were carried out with a Varian Cary Eclipse fluorescence spectrophotometer. The slit-widths were adjusted at 5 nm both for excitation and emission and the photomultiplier was set to operate at high voltage (slit-widths of 2.5 nm were used where the intensity of fluorescence was “over range”). The fluorescence spectra were corrected for both variations with wavelength of the lamp intensity and the photomultiplier sensitivity. Absorbance was commonly too high to use 90° geometry and no fluorescence was observed for PCBs using a triangular cell with front face geometry. Emission is observed when the cell is rotated clockwise 90° with respect to the front face geometry (Fig. 1). Therefore this geometry was chosen for recording the fluorescence of PCBs for this study. UV–Visible absorption spectra were recorded with an HP 8452-A diode array spectrophotometer. In order to prevent excessive inner filter effects, absorbance of all the solutions was matched to 0.100 by adjusting concentrations in a 1 cm cell, which corresponds to absorbance less than 0.1 in the triangular cell used. Solvent emission was also scanned at all wavelengths. Significant solvent emission was not observed at any wavelength of excitation.

2.2.2. Reaction quantum yield measurement

Experiments were carried out in two systems. For tunable wavelengths, irradiation was carried out on a Perkin-Elmer 650-10 S fluorescence spectrophotometer equipped with a 150-W xenon lamp and a grating monochromator. Using the maximum slit width, approximately monochromatic light was obtained with a band width observed to be ~20 nm. In runs, 1.5 ml of PCB 138 (or PCB 77) in 0.1 N alkaline 2-propanol or in 2-propanol alone was pipetted into a regular 1 cm quartz cuvette. Throughout the photolysis, filtered nitrogen in a fine stream was bubbled into the solutions to deaerate the solution and to ensure sample homogeneity and uniform extent of reaction in the light path. During the irradiation experiments, the solution temperatures were controlled by circulating water at a constant temperature (23 °C).

For the two representative (ortho and non-ortho) PCBs, two different wavelengths of excitation were chosen. PCB 138 was irradiated at 254 nm and 290 nm corresponding to excitation at the main band and k band respectively (see Section 4). For PCB 77 the two wavelengths of excitation, 264 nm and 294 nm, correspond to excitation at the two ends of the k band. The main band of PCB 77 is located between 210 and 235 nm and in this range the intensity of the xenon lamp is very low and experimental results in this wavelength region were inconclusive.

Alternative experiments were performed in a Rayonet reactor using a symmetrically placed pair of either 254 nm Hg lamps or 300 nm fluorescent lamps. In these experiments, 2 ml of PCB solutions in either 0.1 N alkaline or in neutral 2-propanol was pipetted into a cylindrical quartz tube with the inside diameter of 1.70 cm. The solutions were deaerated by N_2 bubbling before irradiation, and a magnetic stirrer was used to ensure the homogeneity of the samples. PCB 138 samples were irradiated for 1 min and those of PCB 77 for 3 min.

For both series of experiments, the intensity of light entering the reaction vessels was measured at different wavelengths before and after each experiment using ferrioxalate actinometry [12]; the same geometry and volume of actinometer solution were used with both wavelengths. In so far, as it was consistent with enough irradiation time to be recorded accurately, maximum conversions (PCB reacted) were kept below 10% to avoid inner filter effects of the photoproducts. Concentrations of PCBs (based on the molar absorptivity for a 10 nm band around the excitation wavelength) were such that >99% of the incident light was absorbed.

The samples were analyzed using an Agilent 6890 series gas chromatograph (GC) with an electron capture detector equipped with a DB-608 column (30 m length, 0.25 mm ID, and 0.25 μm film thickness). The GC conditions and the temperature program were chosen as previously reported [13].

3. Results

3.1. Measurement of fluorescence intensity at different wavelengths of excitation

According to Eq. (1), fluorescence intensity is proportional to the intensity of the exciting light, optical density of the solution and the quantum yield of the fluorescence.

$$I_f = I_0(\varepsilon cl)\Phi_f \tag{1}$$

In this equation I_f is the measured fluorescence intensity, I_0 the measured intensity of excitation, ε the molar absorptivity, c the molar concentration, l the path length and Φ_f the fluorescence quantum yield. If the light intensity is corrected for different wavelengths and, if the optical density of the sample at the anticipated wavelengths is the same, intensity of the fluorescence is only dependent on the quantum yield of the fluorescence. Commonly, fluorescence yields are independent of the wavelength of the exciting light (Kasha–Vilvo law). This arises when internal conversion is the dominating mode of deactivation of higher excited states of organic molecules, so that all other processes take place only after the molecules have reached the lowest vibrational level of the lowest excited state of each multiplicity, i.e., usually the S1 and T1. Thus the quantum yield of the various processes in excited molecules, such as fluorescence emission is normally found to be independent of excitation wavelength. But if the internal conversion is slow, competing processes can be significant which makes the fluorescence, wavelength dependent. Hochstrasser reported striking exceptions to the Kasha–Vilvo law for several double aromatic molecules because of their slow internal conversion [14].

Exploring the wavelength dependence of fluorescence, the fluorescence intensities of 12 different PCBs (with 2–6 chlorine atoms) in 2-propanol at different wavelengths were measured. Considering the UV spectrum of each PCB, several wavelengths of excitation corresponding to different points on the two electronic bands (commonly denoted main- and k-band) were chosen and the fluorescence intensity for each excitation wavelength was measured.

The maximum of the absorption bands and approximate molar absorbance for each wavelength as well as the maximum of fluorescence and related intensities at different wavelengths of excitation for the selected PCBs are reported in Table S1 (see supporting material). Excitation and emission slits of 5 nm are optimal for a majority of measurements, but if the intensity of fluorescence was high, slit widths were reduced to 2.5 nm.

Our results suggest that PCBs with Cl atoms at ortho positions exhibit much lower fluorescence than non-ortho PCBs. There is no general rule for the intensity of the fluorescence at different excitation wavelengths for ortho chlorinated PCBs but for non-orthos there is enhancement of the fluorescence, when the excitation is in the long wavelength tail, near the 0–0 transition. This is in agreement with the results obtained in acetonitrile by Belfatmi et al. [15], and in micellar media by Gaecía et al. [16].

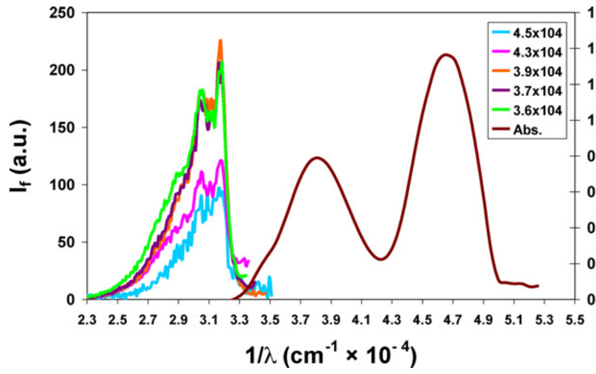

Fig. 2. Absorption spectrum and emission spectra of PCB 77 at different excitation wavelengths. The energy scale, 1/λ, is in wave numbers. Curves of different colors represent different wavelengths of excitation except for the curve at higher energy describing absorbance. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Although the fluorescence intensity of PCBs at different excitation wavelengths differed, one cannot rely on the results reported in Table S1 (supplementary material) as indicative of fluorescence yield trends. This is because the fluorescence measurements were performed at different concentrations and under different light intensities, which were instrumentally unavoidable. On the other hand looking at the fluorescence spectra reported in Fig. S1 (supplementary material) for some PCBs the shapes of fluorescence spectra recorded at different excitation wavelengths are different. This property can be more reliably used to elucidate the characteristics of the excited state.

Figs. 2 and 3 show the actual absorption spectra of PCB 77 and of PCB 138 and overlay fluorescence spectra at different wavelengths of excitation. The scale is chosen to be proportional to energy so that band shapes can be compared to theory. The spectra of the remainder of the congeners studied are found in Figs. S1–S5 of the supplementary material. The possibility that the variation in fluorescence line shapes was a consequence of reaction occurring under the illumination of the spectrofluorometer was eliminated by repeating scans after a delay.

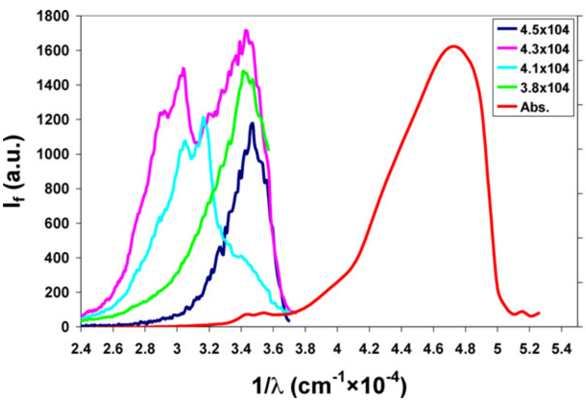

Fig. 3. Absorption spectrum and emission spectra of PCB 138 at different excitation wavelengths. The energy scale, 1/λ, is in wave numbers. Curves of different colors represent different wavelengths of excitation except for the curve at higher energy describing absorbance. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

3.2. Quantum yields of the reaction at different wavelengths

3.2.1. Medium alkaline 2-propanol

Preliminary experiments for the estimation of the apparent reaction quantum yields were undertaken for the alkaline solutions of two key congeners, PCB 138 and PCB 77, representatives of ortho and non-ortho PCBs. These are the conditions used to produce the chain reaction of applied interest. The samples were irradiated at different wavelengths using the xenon lamp of a spectrofluorometer. Data for the comparison are provided in Table 1.

From these experiments and comparison with values published in literature, it was realized that the quantum yields are dependent on the concentration of PCBs and on the intensity of light. Therefore the quantum yields reported in Table 1 are at best ‘conditional’ apparent yields. This is because the absorbance matched initial concentrations are not the same for each PCB. Further, the light source is a xenon lamp with different light intensities at different wavelengths with the lowest light intensity at 254 nm or 264 nm.

We considered, then, the need to compare apparent quantum yields at the same concentration of PCB and under the same light intensity. In such a comparison, it is also necessary to assure that both congeners are absorbing >95% of incident light. The only option available is to use lamps of near monochromaticity at the same intensity. This can be achieved with a low pressure Hg lamp for 254 nm and a fluorescent coated lamp for 300 nm choosing a number of bulbs to match light intensity (the light intensities at these two wavelengths were very close with the same number of lamps). The results are summarized below. In these experiments, the observed yields were close at both wavelengths (Table 2).

These reactions were performed in alkaline 2-propanol, therefore along with direct dechlorination, a chain reaction is also involved. Further, under this condition the rate of the reactions is high and it is not possible to keep the percent conversion of the PCB less than 10%. Since the primary goal was to study the nature of the excited state, not the details of the application, it is preferable to eliminate the (non-photochemical) chain reaction part by performing the experiment in neutral 2-propanol.

3.2.2. Medium neutral 2-propanol

The results of two series of experiments in neutral conditions (no chain propagation) are summarized in Table 3. Again the experimental options were severely limited by the requirement to match concentrations and intensities at the two wavelengths.

This table indicates variation of quantum yield of reactions with variation of the wavelengths. Supporting evidence comes from the product distributions. Product distributions for PCB 77 and for PCB 138 in 0.1 N alkaline 2-propanol at 254 nm and 300 nm were compared and the results are shown in Table 4; because the reaction for PCB 138 at 254 nm is very fast, light intensity was cut in half to get a comparable percent degradation to the reaction at 300 nm.

4. Discussion

4.1. Comparing the fluorescence band shapes and the reaction quantum yields at different excitation wavelengths

4.1.1. Interpreting the florescence spectrum

The key task is to compare the shapes of the fluorescence spectra at different excitation wavelengths since these can respond to subtle variations of vibronic structure of excited states and reveal emission origins from subtly varying states. In general fluorescence and absorption characteristics of an aromatic compound can provide qualitative information concerning the conformation of the chromophore in the ground state, as well as that in the excited state [17]. The absorption and the fluorescence spectra can be compared in terms of the Stoke’s shift and by their shapes. If the Stoke’s shift is large and the shapes of the absorption and fluorescence spectra are not mirror images, one can conclude that the conformation of the molecule in the ground and excited states is significantly different. Spectroscopically, Berlman [18] has classified the fluorescent aromatic compounds into five classes; those whose chromophores are:

1. planar[1] in the ground state and first excited state,
2. non-planar in both states with the geometry preserved,
3. non-planar in the ground state but increasingly planar in the excited state,
4. non-planar in the ground state and increasingly non-planar in the excited state,
5. planar in the ground state but non-planar in the excited state.

For each class of molecules he has also listed the fluorescence characteristics (the shape and intensity), therefore one might assign the geometry of the ground and excited states of a molecule by matching the observed fluorescence properties with the ones cited by Berlman [18]. Little has been published analyzing fluorescence characteristics of PCBs in detail, but the fluorescence characteristics of the parent compound, biphenyl, have been subject of extensive qualitative and quantitative studies. This provides a useful model for the difference between ground and excited state conformations.

4.1.1.1. Biphenyl (BP) and PCBs. The BP absorption spectrum is broad with no vibrational structure. The emission spectrum, however, is moderately structured. There is also a large Stoke’s shift, which implies quite significant conformational change on excitation. BP is a class three molecule (non-planar in the ground state and planar in the excited state). Because of the interaction of hydrogens at ortho positions, BP prefers a non-planar configuration in its ground state. The added resonance interaction between the rings in the excited state, the rise of double bond character, forces the rings into a more planar configuration [18,19]. Moving from biphenyl to PCBs, the interactions of the two benzene rings can be influenced by the number and position of the chlorine substituents. Different isomers exhibit varying degrees of steric hindrance affecting their fluorescence spectra. Based on the shape and intensity of the fluorescence one can assign the class of compound, but we will see that fluorescence shape depends on excitation wavelength.

So far the difference between PCB isomers, in terms of the configuration of the excited state based on analysis of fluorescence properties has not considered wavelength of excitation. For biphenyl, Naqvi et al. [20] reported in 1975 that the shape of the fluorescence spectrum of BP is sensitive to excitation wavelength. They suggested that as excitation wavelength increases the excited state population becomes richer in planar and nearly planar conformers. In 1982, Fuji et al. [21] quantitatively interpreted the wavelength dependence of fluorescence of BP in terms of the intramolecular geometric relaxation about the central C–C bond, as a function of solvent viscosity and temperature. They classified the processes of the intramolecular geometric relaxation of biphenyl into five contributors: (1) vibrational relaxation, (2) emission without geometric relaxation, (3) geometric relaxation along the twist angle between the planes of two benzene units of biphenyl (θ), (4) emission from incompletely relaxed conformers, (5) emission from a completely relaxed conformers. Process 3, rotation about the C–C bond, was considered to be rate determining. It appeared that depending on excitation wavelength, different conformers with

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[1] The term planar is approximate, literally true in some cases like biphenyl models, but used in this case as a relative term.

Table 1
Apparent quantum yield of the reaction (Φ_r) for PCB 77 and PCB 138 at two different wavelengths of excitation. All quantum yields were measured in alkaline 2-propanol under deaerated condition. These experiments were performed in a spectrofluorometer.

PCB #	[PCB] (M)	$\lambda_{exci.}$ (nm)	Irradiation time (min)	I_0 (photons/s)	% deg.	Φ_r
77	1.19×10^{-4}	264	55.0	1.49×10^{14}	8.4	0.024 ± 0.02
77	8.10×10^{-4}	294	1.5	4.91×10^{14}	12.4	2.74 ± 0. 20
138	3.74×10^{-5}	254	60.0	1.63×10^{13}	6.1	0.047 ± 0.05
138	1.00×10^{-3}	290	7.0	5.74×10^{14}	6.2	0.43 ± 0.04

Table 2
Apparent quantum yield of the reaction (Φ_r) for PCB 77 and PCB 138 at 254 nm and 300 nm. All quantum yields were measured in alkaline 2-propanol under deaerated condition. These experiments were performed in a Rayonet photoreactor.

PCB #	[PCB] (M)	$\lambda_{exci.}$ (nm)	Irradiation time (s)	I_0 (photons/s)	% deg.	Φ_r
77	3.42×10^{-4}	254	15	1.68×10^{16}	21.8	1.63 ± 0.05
77	3.42×10^{-4}	300	15	1.03×10^{16}	17.9	1.74 ± 0.08
138	5.26×10^{-4}	254	15	1.62×10^{16}	68.6	6.60 ± 0.30
138	5.26×10^{-4}	300	15	1.06×10^{16}	61.5	6.10 ± 0.30

Table 3
Apparent quantum yields of the reaction for PCB 77 and PCB 138 at 254 and 300 nm. All quantum yields were measured in neutral 2-propanol under deaerated condition and the experiments were performed in a Rayonet photoreactor.

PCB #	$\lambda_{exci.}$ (nm)	[PCB] (M)	Irradiation time (min)	I_0 (photons/s)	% deg.	Q.Y.	Q.Y. ratio[a]	Q.Y. ratio[b]
138	254	9.50×10^{-4}	1.0	1.12×10^{16}	8.9	0.38 ± 0.03	–	(1.93), 2.47
138	300	10.7×10^{-4}	1.0	1.16×10^{16}	12.1	0.56 ± 0.05	1.48	(2.05), 2.73
138	254	4.90×10^{-4}	1.0	1.25×10^{16}	7.8	0.15 ± 0.02	–	–
138	300	5.23×10^{-4}	1.0	1.23×10^{16}	9.6	0.21 ± 0.02	1.34	–
77	254	5.17×10^{-4}	3.0	1.25×10^{16}	8.1	0.057 ± 0.002	–	(1.88), 1.54
77	300	5.30×10^{-4}	3.0	1.23×10^{16}	5.9	0.042 ± 0.004	0.74	–
77	254	2.74×10^{-4}	3.0	1.12×10^{16}	8.9	0.037 ± 0.004	–	–
77	300	5.68×10^{-4}	3.0	1.16×10^{16}	5.7	0.044 ± 0.004		(1.07), 1.05[c]

[a] Quantum yield ratios at the same concentration but at different λs (300/254).

[b] Quantum yield ratios at different concentrations but at the same λs. Numbers in parentheses in this column are ratios of concentration.

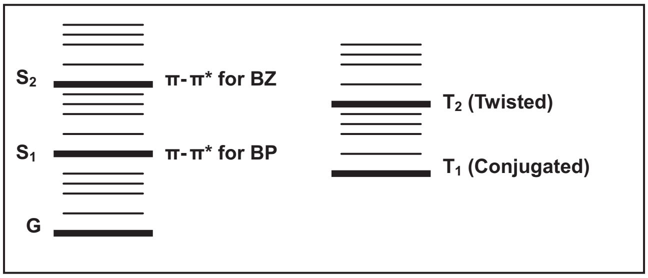
[c] This value tests precision since it is ~1 in principle.

Table 4
Selected product distribution for PCB 77 (20 ppm) and PCB 138 (20 ppm) using 254 and 300 nm light sources in the Rayonet photoreactor. λ irrad.: wavelength of irradiation. PCB? is a congener, which appears at the same retention time in both cases.

PCB	λ irrad.	% degradation	Product distribution		PCB	λ irrad.	% degradation	Product distribution	
			PCB (congener)	% produced				PCB (congener)	% produced
77	254 nm	69.4	35	13.6	77	300 nm	70.0	35	18.9
			37	6.5				37	8.1
138	254 nm	53.7	35	0.6	138	300 nm	55.6	35	0.7
			99	1.4				99	0.9
			77	5.9				77	7.1
			118	17.4				118	15.4
			105	0.8				105	1.2
			PCB ?	3.7				PCB ?	2.9

different rotation angles (θs) are excited, which leads to different distributions of conformers in the excited state. If process 3 is complete before emission, fluorescence originates from the relaxed excited conformers and fluorescence is independent of the excitation wavelength. Where the fluorescence spectrum varies with the excitation wavelength, incompletely relaxed conformers are important. Moreover, intersystem crossing rate constants could be observed to depend on excitation wavelength by freezing conformers at low T in glasses. Pursuing the analogy to BP is relevant to speculation about involvement of singlet excited states in dechlorination of PCBs.

To appreciate the analysis, recall the origin of the absorption bands of PCBs (Scheme 1). S_1 originates from a π–π^* transition of biphenyl (k band) which requires some conjugation of the two benzene rings and S_2 is related to the π–π^* transition of individual benzene rings (main band). The k band is well resolved in the absorption spectra of non ortho, mono ortho and is a weak band for di-ortho PCBs. Therefore, for these groups of PCBs, the excitation is assumed to increase conjugation with respect to the ground state. Therefore these congeners have a more conjugated, hence more nearly planar excited state conformation, like BP. But, if more than



Scheme 1.

Table 5
Effect of light intensity on quantum yield of the expected chain reaction. Data from reaction in the Rayonet and reaction in spectrofluorometer (Spect.) are compared; PCBs are in alkaline 2-propanol.

PCB #	[PCB] (M)	Reactor	$\lambda_{exci.}$ (nm)	I_0 (photons/s)	% deg.	Φ_r
77	1.19×10^{-4}	Spect.	264	1.49×10^{14}	8.4	0.024 ± 0.02
77	3.24×10^{-4}	Rayonet	254	1.68×10^{16}	21.8	1.63 ± 0.05
77	8.10×10^{-4}	Spect.	294	4.19×10^{14}	12.4	2.74* ± 0.20
77	3.42×10^{-4}	Rayonet	300	1.03×10^{16}	17.9	1.74 ± 0.08
138	3.74×10^{-5}	Spect.	254	1.63×10^{13}	6.1	0.047 ± 0.05
138	5.26×10^{-4}	Rayonet	254	1.68×10^{16}	35.2	6.60 ± 0.30
138	1.00×10^{-3}	Spect.	290	5.74×10^{14}	6.2	0.43 ± 0.04
138	5.26×10^{-4}	Rayonet	300	1.03×10^{16}	34.5	6.05 ± 0.30

two ortho chlorines are present in ortho positions, the expected symmetry of the excited singlet state of PCB would be S_2 with a twisted conformation. Thus upon excitation to S_1 and S_2 both conjugated and strongly twisted forms could be involved in the excited states. The diagnostic assumption [18] is that if a highly twisted configuration is involved then the fluorescence spectrum will be unstructured, but where structured emission is observed, photons are emitted from an excited state with central C–C conjugation.

4.1.1.2. Fluorescence spectra of PCB 77 and PCB 138 at different wavelengths. Overall, fluorescence spectra of PCBs (see Figs. S1–S5) show that the fluorescence behavior of non ortho PCBs is similar to that of BP. These non ortho isomers and/or PCB isomers with substituents symmetrically placed on the long axis of the molecule [20] have the highest relative fluorescence intensity. For others, as excitation wavelength increases, the excited state population appears to become richer in more conjugated (quasi-planar) conformers. In the following the focus is on the fluorescence behavior of PCB 77 and PCB 138.

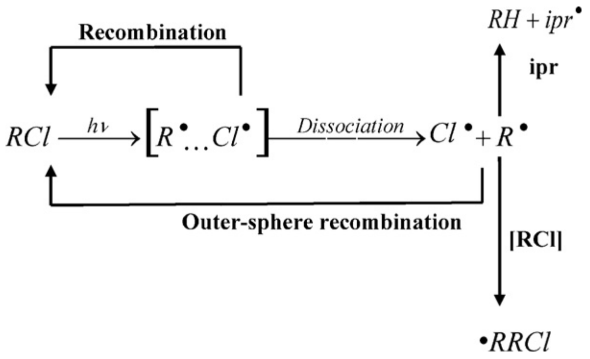
PCB 77: For PCB 77 (Fig. 2) the shape of the fluorescence spectrum at different wavelengths does not depend on the wavelength of excitation, which is similar to that of BP. For BP there is a quite significant geometrical distortion upon excitation. This could be the case for PCB 77. To verify distortion, the fluorescence spectra of deuterated and non-deuterated forms of this congener were compared at several selected wavelengths in a range from 226 nm to 274 nm. The results show no significant difference between H and D. This can be explained by strong coupling of the ground state and excited state following the large geometric change between the ground and excited states. It seems more likely that excited PCB 77 relaxes rapidly from a twisted conformation to a more planar structure and readily crosses to the triplet excited state, which reacts. This tends to be confirmed by the fact that PCB 77 photolysis is more completely quenched by given oxygen levels than ortho PCBs [13].

PCB 138: In case of PCB 138 (Fig. 3), the shape of the fluorescence spectrum is sensitive to wavelength of excitation. At different excitation wavelengths, different conformers are excited. Process 3 (geometric relaxation along θ) must also be slow to observe signals from different conformations (conjugated, twisted and more twisted; exhibiting different vibrational level patterns). This is expected where the rate of internal conversion is slow and not all molecules are relaxed to the lowest vibrational excited state. Two obvious factors are involved in this unusual case. The steric hindrance from ortho chlorines retards rotational relaxation around the C–C bond, as does the solvent. It is important to recall that all the structures in BP spectra could be quantitatively modeled by considering only the coordinate for rotation around the central C–C bond.

An oxygen quenching experiment was attempted in order to estimate the lifetime of the singlet excited state of PCB 138. But PCB 138 was subject to at most a limited fluorescence quenching by oxygen and reliable determination of the Stern–Volmer slope was not possible. A test was performed for PCB 15. PCB 15 shows a hint of the shape dependence on excitation wavelength that reaches an extreme in the case of PCB 138. For this purpose, the fluorescence intensities were measured for three solutions: deaerated, non deaerated (P_{O_2} ~0.2 atm) and O_2 saturated (P_{O_2} ~1). The results show that while the fluorescence of PCB 15 is quenched by oxygen, there is also a non-quenchable part (fast fluorescence). Assuming diffusion limited quenching, the fluorescence lifetime of PCB 15 was estimated to be ~300 ns. This places an upper limit on the lifetime of PCB 138 at no more than ~150 ns. Therefore a prompt photochemical reaction can happen from a higher vibronic level of the excited state rather than relaxing to the lowest vibrational level first, and/or crossing to a triplet state. This may offer insight into failure of complete quenching of reaction at limiting oxygen concentrations [13]. The next section deals with the data on quantum yields.

4.2. Quantum yield variation over a narrow spectral region

Table S2 in supplementary material (summarizing available PCB photophysical and photochemical data) was prepared in a search for evidence of excitation wavelength dependence. These data, reported by different groups, cannot be directly compared for several reasons: different light sources have been used; some experiments are performed in deaerated conditions some not, different initial concentrations of PCBs have been used and more importantly different methods (e.g. disappearance of the PCB congeners at a certain conversion, biphenyl production or release of chloride ion) have been applied to reporting quantum yields. Differences in solvent and type of actinometer used are also factors [22]. The main lesson of the wide variations reported is that attention should be given to concentration of PCBs and light intensity. Nevertheless, the similarities expected in several cases between two solvents or two wavelengths of excitation compared to the wide variation in quantum yields reported first led to examination of concentration and intensity dependence of quantum yields (see next section) and this surely accounts for much of the surprising variations. The consequence is that the literature hinted at but did not provide a clear case for variation of yield with excitation wavelength. Therefore a direct comparison, with parallel measurements of the quantum yields of PCB 77 and PCB 138 under controlled conditions was required. The results are shown in Table 3. Based on the results for the experiments performed in neutral 2-propanol, the apparent quantum yields at different wavelengths superficially appear to be different. The uncertainty of the measurements is the estimated systematic error, which may be greater than the limit of precision. The uncertainty leaves us with some ambiguity. However, comparing product distributions at 254 nm and 300 nm for approximately the same percent degradation (results reported in Table 4), appears to confirm different apparent yields at different wavelengths.



Scheme 2. Major reaction pathway.

4.2.1. *Dependence of quantum yield of the reaction on concentration and light intensities in the case of the chain reaction*

As discussed above with respect to careful analysis of reaction in neutral IPA, there is evidence that the quantum yields of the reactions are dependent on initial concentration of PCBs and the intensity of light sources. In alkaline IPA, where the chain reaction is important, the dependence on initial concentration can be seen in Table 5. Intensity dependence emerges from comparing the results performed in the Rayonet to those run with the spectrofluorometer.

This comparison shows that the generally higher concentration or light intensity, gives higher 'conditional' apparent quantum yield (the only problematic case, denoted with a * in Table 5, is quantum yield of PCB 77 measured in the spectrofluorometer at 294 nm which is higher than that run in the Rayonet at 300 nm). It appears that unambiguous evidence for quantum yields greater than one such as those reported earlier (1) and essential to the practical applications (9) arise only for relatively high intensity, and that the chain reaction may only be significant under these conditions. This result is important to applications.

The commonly assumed chemical reaction pathway following upon excitation as summarized in Scheme 2 may be used to conceptualize possible effects of light intensity and concentration.

First homolytic bond scission occurs within the solvent cage, cage recombination of the primary radicals occurs to some degree (since 2-propanol is the solvent and adjacent to the radical pair, one cannot exclude extraction of H by the paired aryl radical). Those radicals that escape from the solvent cage can abstract hydrogen from solvent 2-propanol to produce product PCB and an isopropanol radical (iPr•). Remaining fates are (1) outer sphere recombination to restore that starting PCB, and (2) reaction with solutes such as other PCB molecules. Intensity dependence might arise from increasing steady state concentrations of radicals, implying radical capture by IPA competes with outer sphere recombination and such recombination is important at low intensity. PCB concentration dependence would seem to require a contribution from the pathway involving PCB concentration or from PCB forming either a ground state dimer or an eximer. Unfortunately, none of the spectroscopic probes yield any evidence for this and relevant concentrations are two low for colligative property determinations to detect any dimerization.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2011.04.028.

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