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Journal of Photochemistry and Photobiology A: Chemistry 91 (1995) 81–85

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A:CHEMISTRY

Photosensitized dechlorination of polychlorinated phenols
1. Carbazole-photosensitized dechlorination of pentachlorophenol

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Received 10 August 1994; accepted 3 May 1995

Abstract

The dechlorination of pentachlorophenol (PCP) photosensitized by carbazole (Cz) has been studied. It is shown that 2,3,4,5,-tetrachlorophenol (TCP) is the main primary product. Prolonged irradiation results in the formation of trichlorophenols. The process is explained via a mechanism involving electron transfer from excited Cz to PCP.

Keywords: Carbazole; Dechlorination; Electron transfer; Fluorescence quenching; Pentachlorophenol; Photochemical reaction

1. Introduction

Polychlorophenols represent an important class of compounds because of their widespread practical applications. They are very useful as pesticides, germicides and fungicidal agents. Unfortunately, they are very toxic and their accumulation in the environment, especially in water sources, is a growing problem [1].

One of the methods used for the purification of water is photochemical destruction of the impurities induced by UV light. Unfortunately, this treatment cannot be recommended for the purification of water containing phenols, especially pentachlorophenol (PCP). It has been demonstrated that the irradiation of PCP in water results in the formation of dibenzo-*p*-dioxins and polychlorinated dibenzofurans, compounds considerably more toxic than PCP [2,3].

Photosensitized oxidation of polychlorophenols was suggested as a possible solution to this problem [4–9]. The process was found to occur with the participation of singlet oxygen. The efficiency of photo-oxidation is strongly dependent on the polarity of the solvent used and on the pH in the case of aqueous solutions [5].

It is well known that the toxicity of polychlorinated aromatics decreases with a decrease in the amount of chlorine substituents present in the molecule. Thus dechlorination of the molecule could be an alternative approach to the problem. It has been shown that the photodechlorination of polychlorinated biphenyls can be efficiently photosensitized by naphthalene [10]. The process involves electron transfer occurring via an exciplex intermediate. This paper reports our studies on the dechlorination of pentachlorophenol photosensitized by carbazole (Cz).

2. Experimental details

2.1. Materials

Pentachlorophenol (Aldrich, 99%), 2,3,5,6-tetrachlorophenol (Aldrich, 98%), 2,4,6-trichlorophenol (Aldrich, 98%), 2,4,5-trichlorophenol (Aldrich, 99%), 2,5-dichlorophenol (Aldrich, 98%) and 2,4-dichlorophenol (Aldrich, 99%) were used as received. Phenol (99+%) was purified by sublimation. Carbazole (Aldrich, 99%) was recrystallized twice from benzene. Acetonitrile (Aldrich, high performance liquid chromatographic grade), heptane (Merck, spectrophotometric grade) and methanol (Aldrich, spectrophotometric grade) were used without further purification. Hexane (Reachim, pure) was distilled before use.

2.2. Procedure

2.2.1. Irradiation of samples

All samples were irradiated in a Rayonet photochemical reactor (model RPR-100) equipped with 16 RPR-3500 lamps, 24 W each. The intensity of the incident light produced by one lamp was approximately (1.5–5) × 10^{16} photons s^{-1} cm^{-3} as stated by the manufacturer. Solutions of PCP ($c = 10^{-3}$–10^{-2} mol dm^{-3}) as well as mixtures of PCP and Cz in MeCN (both 10^{-3} mol dm^{-3}) were deoxygenated by

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bubbling with argon for 15 min prior to irradiation. The temperature in the irradiation chamber was around 40 °C.

2.2.2. *UV–visible spectra*

UV–visible absorption spectra of the samples were measured at room temperature using a Shimadzu 2101 PC spectrophotometer.

2.2.3. *Infrared spectra*

IR spectra of the samples were recorded at room temperature on a Bruker IFS 48 spectrophotometer.

2.2.4. *Fluorescence spectra*

Steady state emission and excitation spectra were measured at room temperature on an MSF 102 spectrofluorimeter.

Fluorescence decay curves were measured using a single-photon-counting apparatus. Solutions of Cz ($c=7\times10^{-5}$ mol dm^{-3}) with PCP added as quencher ($c=0$–7×10^{-3} mol dm^{-3}) in heptane and MeCN were degassed by multiple freeze–pump–thaw cycles. The samples were excited at 313 nm and the emission at 365 nm was measured.

2.2.5. *Gas chromatography (GC)–mass spectrometry (MS) analysis*

The products formed upon irradiation were analysed using a Hewlett–Packard 5890 GC–MS instrument equipped with an HP-1 capillary column (12 m, 0.20 mm inner diameter, 0.33 μm film thickness). The parameters of the analysis were as follows: split ratio 1:38, carrier gas helium at 0.5 ml min^{-1}, injector temperature 280 °C, detector temperature 280 °C. The oven temperature programme was from 60 °C for 2 min to 260 °C for 2 min at 10 °C min^{-1}. The kinetics of the reaction was followed using an INCO GC-505M gas chromatograph equipped with an electron capture (EC) detector and a DB-5 capillary column (30 m, 0.32 mm inner diameter, 0.25 μm film thickness). The parameters of the analysis were as follows: split ratio 1:13, carrier gas nitrogen at 38.7 cm s^{-1} (1.86 ml min^{-1}), make-up gas nitrogen at 40 ml min^{-1}, injector temperature 270 °C, detector temperature 280 °C. The oven temperature programme was from 130 °C for 30 s to 250 °C at 4 °C min^{-1}.

3. Results and discussion

3.1. *Photochemical reactions of PCP in acetonitrile solution*

Irradiation of PCP solution in MeCN ($c_{\text{ini}}=1\times10^{-2}$ mol dm^{-3}) in the presence of Cz ($c=1\times10^{-2}$ mol dm^{-3}) was performed in an argon atmosphere in the Rayonet photochemical reactor.

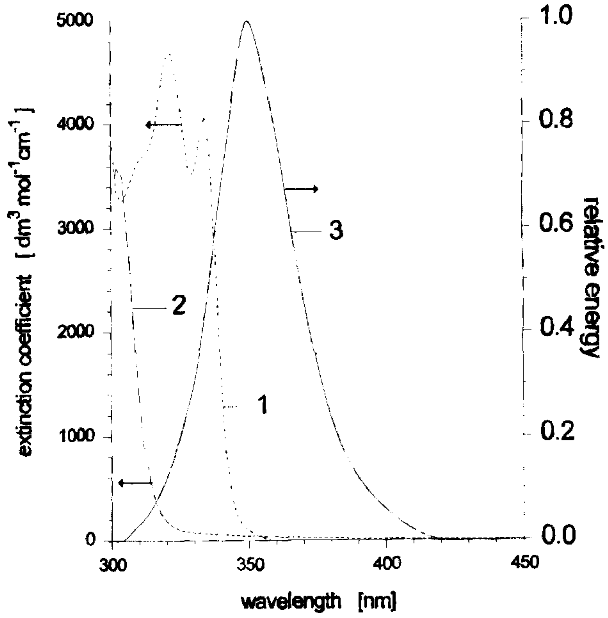
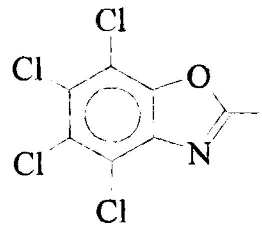


Fig. 1. Electronic absorption spectra of Cz (1) and PCP (2) in MeCN (near-UV–visible spectral region) and spectral distribution of energy characteristic for light source used in photochemical experiments (3).

Fig. 1, which presents a comparison of the absorption spectra of PCP and Cz, shows that the incident radiation is almost exclusively absorbed by Cz. The solution turned yellowish upon irradiation. Analysis of the UV–visible absorption spectra recorded for the solution before and after various times of irradiation (Fig. 2) showed an increase in absorbance in the spectral ranges 250–280 and 300–500 nm.

The photochemical reactions of PCP were also followed by GC analysis. Fig. 3 shows the GC traces obtained for the system before and after irradiation with light at λ = 350 nm. One can observe that the photochemical reactions involve the dechlorination of PCP; the peaks characterized by shorter retention times can be assigned to the phenol containing fewer chlorine substituents. GC–MS analyses have shown that the main primary product is 2,3,4,5-tetrachlorophenol (TCP) which is formed by the removal of chlorine from the ortho position relative to the hydroxyl group. Prolonged irradiation results in the formation of trichlorophenols. Unexpectedly, no less chlorinated phenols nor unsubstituted phenol were detected. GC analysis also showed the formation of some light product of very short retention time which coeluted with the solvent.

It has also been shown that two side products are formed in the reaction mixture. The molecular mass of the first is 271, which matches the molecular mass of 2-methyl-4,5,6,7-tetrachlorobenzoxazole (MTCB):



The formation of MTCB has already been reported during the irradiation of PCP in MeCN solution [11]. The molecular mass of the second compound is 397. This indicates that it

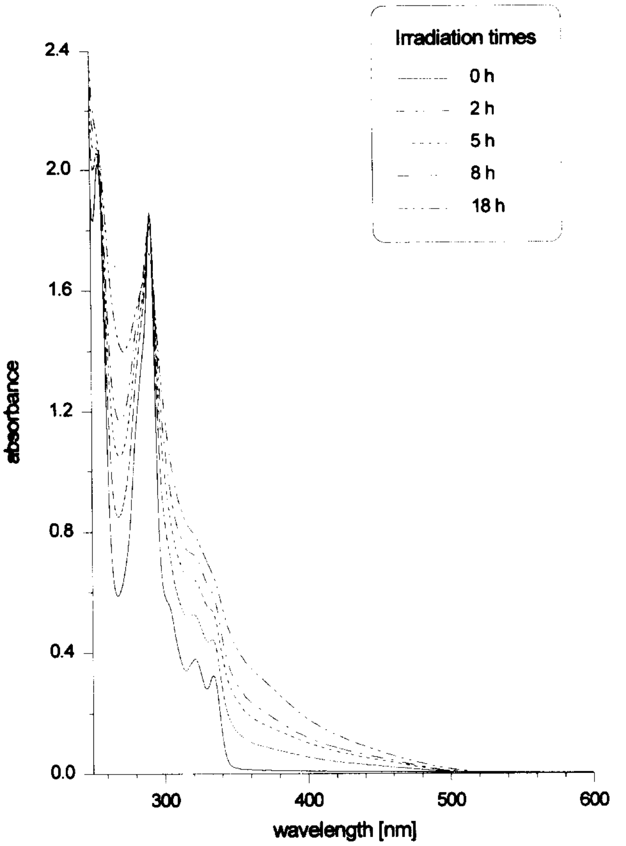
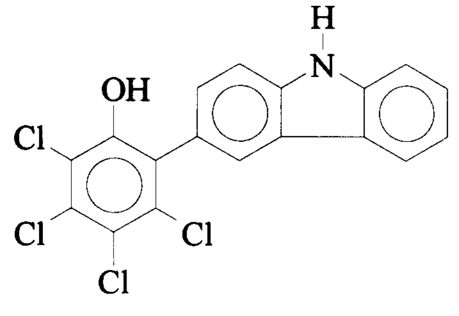
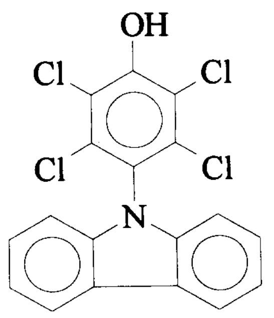


Fig. 2. Electronic absorption spectra of PCP + Cz in MeCN recorded before and after various times of irradiation in argon atmosphere.

might be a product of the condensation of Cz with PCP occurring with the removal of HCl. The presence of the carbazole unit in this compound is supported by the appearance of the 167 u ion in the mass spectrum. There are 15 possible products of this type, e.g.





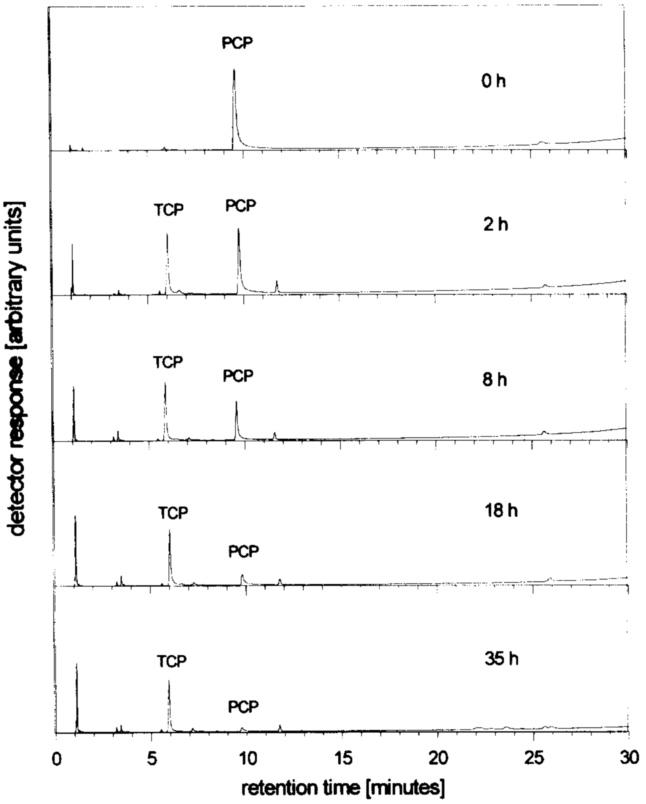


Fig. 3. GC traces for PCP before and after irradiation in presence of Cz in MeCN solution for 2, 8, 18 and 35 h. An electron capture detector (ECD) was used. GC conditions are given in text.

The possible compounds of this type with highly conjugated aromatic structures are probably responsible for the yellowing of the PCP + Cz solutions during irradiation. Fig. 4 illustrates the dependence of the PCP conversion on the irradiation time as well as the fit of the experimental data to the second-order kinetic equation.

3.2. Studies of the mechanism of carbazole-photosensitized dechlorination of PCP

Measurements of the steady state fluorescence spectra of Cz in the absence and presence of PCP in MeCN or heptane solution have shown that PCP efficiently quenches the emission of Cz (Fig. 5). The fluorescence spectra recorded for Cz in the presence of PCP do not display any additional bands even at high concentrations of the components. Measurements of the fluorescence lifetime of Cz in the absence and presence of PCP have confirmed the occurrence of quenching of carbazole molecules in their electronically excited singlet state by PCP. The quenching process can be described by the Stern–Volmer kinetic equation expressed as a dependence of the ratio of the fluorescence intensities (I_0/I) or the ratio of the fluorescence lifetimes (τ_0/τ) of Cz on the concentration of PCP (see Fig. 6). The bimolecular rate constants of quenching of Cz by PCP in MeCN and heptane have been determined experimentally from the slopes of the lines presented in Fig. 6 and are given in Table 1. The values are high

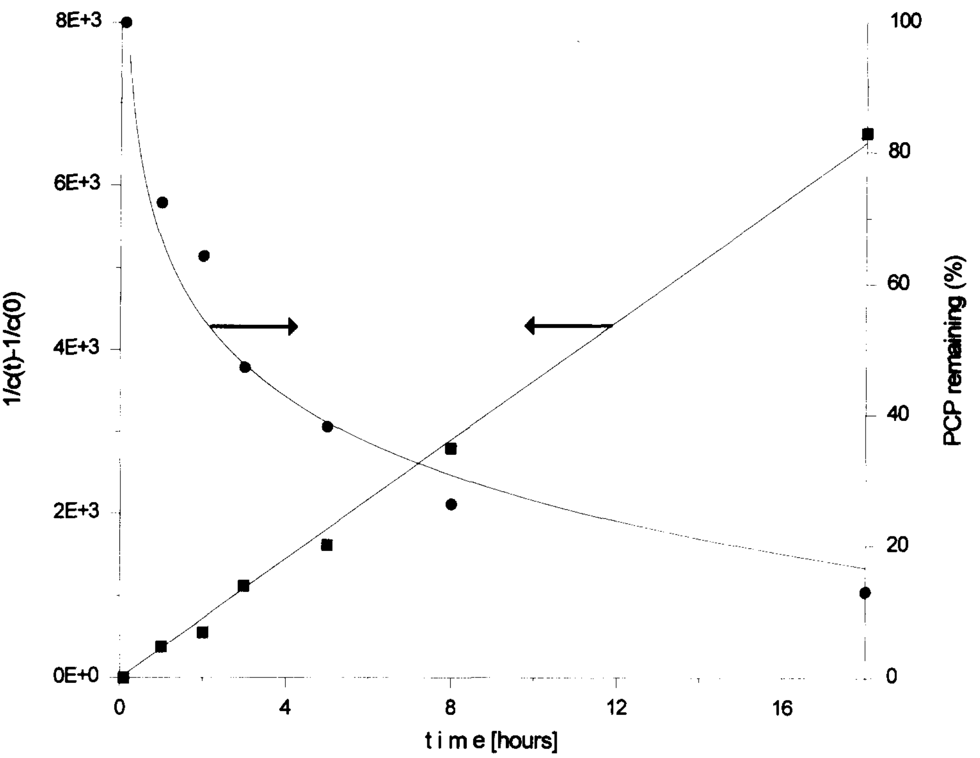


Fig. 4. Dependence of PCP concentration on irradiation time fitted to second-order kinetic equation (■) and dependence of PCP concentration on irradiation time (●).

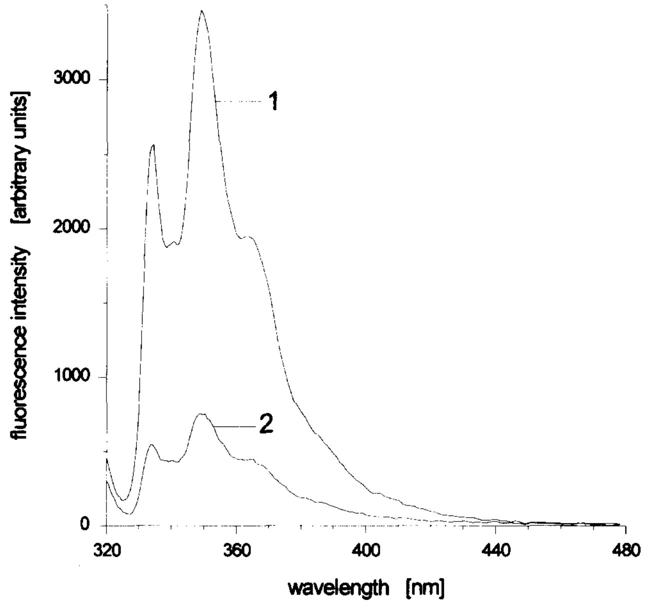


Fig. 5. Steady state fluorescence spectra of Cz in MeCN solution in absence (1) and presence (2) of PCP ($c_{Cz} = 7 \times 10^{-5}$ mol dm^{-3}, $c_{PCP} = 7 \times 10^{-3}$ mol dm^{-3}, $\lambda_{exc} = 334$ nm).

and reach a diffusion-controlled limit in the respective solvents [12]. Data obtained from the steady state measurements in heptane are in a good agreement with those from the measurements of lifetimes. This indicates that the quenching of the excited singlet state of Cz in an inert solvent such as heptane is a collisional dynamic process. The situation is quite different when MeCN is used as solvent. The rate con-

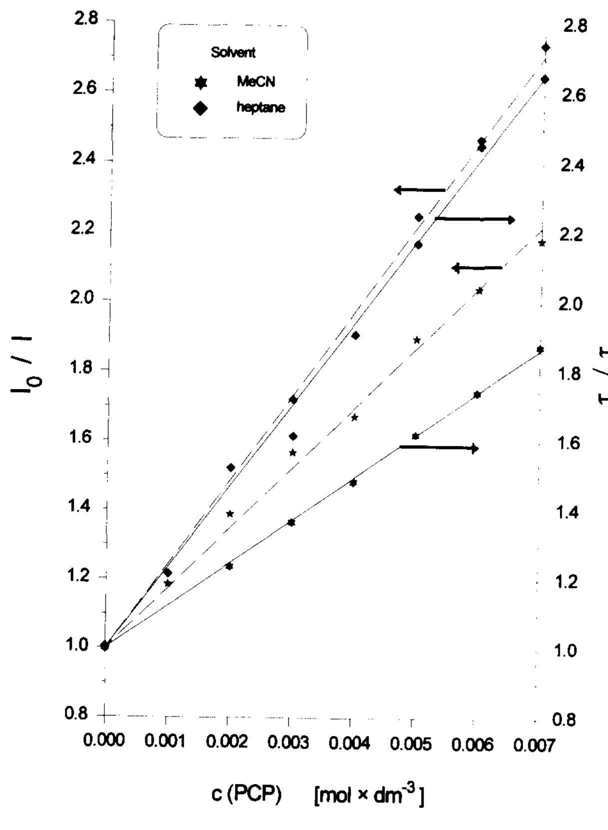


Fig. 6. Stern–Volmer plots of Cz fluorescence quenching by PCP in heptane and MeCN ($c_{Cz} = 7 \times 10^{-5}$ mol dm^{-3}). I_0/I is the ratio of Cz fluorescence intensities in the absence (I_0) and presence (I) of PCP and τ_0/τ is the ratio of Cz fluorescence lifetimes in the absence (τ_0) and presence (τ) of PCP.

Table 1
Rate constants for quenching of Cz excited singlet state in MeCN and heptane solutions determined from steady state data (k_q^S) and lifetime measurements (k_q^τ)

Solvent	k_q^S (10^9 dm^3 mol^{-1} s^{-1})	k_q^τ (10^9 dm^3 mol^{-1} s^{-1})
Heptane	15.2 ± 0.4	15.5 ± 0.4
MeCN	11.6 ± 0.2	8.2 ± 0.1

stants determined by these two methods are considerably different: the value obtained from the steady state measurenents is higher than that from the kinetic treatment and may ndicate the occurrence of specific interactions in the system. t has been shown that there are no new bands in the absorpion and excitation spectra of the mixture of Cz and PCP, only those characteristic of the components of the mixture. This tends to suggest that there is no ground state complexation between Cz and PCP. Taking into account the abovementioned facts, it seems reasonable to suggest that the observed discrepancies in the values of k_q result from the nvolvement of the solvent (MeCN) in the photophysical processes occurring in the Cz + PCP system. This might explain the appearance of MTCB, a side molecular product of the photochemical reaction occurring in the reaction mixture.

On the basis of the absorption and emission spectra of PCP in MeCN, the energy level for PCP in its first excited singlet state was determined to be about 93.3 ± 0.3 kcal mol^{-1}. Since the energy of the first excited singlet state of Cz is 84.8 kcal mol^{-1} [12], the energy transfer from Cz to PCP should be negligible. The most probable mechanism of the fluorescence quenching of Cz by PCP is electron transfer.

The above observation is consistent with previous reports. It has frequently been reported that the fluorescence of aromatic compounds is quenched by molecules with higher excited singlet states [13–15]. The process was rationalized in terms of exciplex intermediate, although no exciplex emission has been observed. It was demonstrated that the mechanism of the quenching of Cz fluorescence in 3-methylpentane solutions by halocarbons involves charge transfer [15]. Thus it can be suggested that the most probable mechanism of the carbazole-photosensitized dechlorination of PCP is an electron transfer followed by the formation of a radical anion of PCP, which releases a chlorine anion.

4. Conclusions

Carbazole in acetonitrile solutions efficiently sensitizes the dechlorination of pentachlorophenol. The reaction seems to involve an electron transfer from the electronically excited carbazole to the PCP molecule and the release of a chlorine anion. Since, in addition to tetrachlorophenols, trichlorophenols are also produced at longer irradiation times, this mechanism may also be valid for less chlorinated phenols.

Acknowledgements

The authors are grateful to Professor M. Najbar and Ms. B. Gałuszka for their help with the GC–MS analysis and to the Polish State Committee for Scientific Research for financial support in the form of research grant PB 1114/P3/92/02.

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