Photodechlorination of PCB's in the Presence of Titanium Dioxide in Aqueous Suspensions

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INTRODUCTION

In view of their biological and chemical stability, the photoreactions of polychlorobiphenyls (PCB's) may be a significant route for their environmental degradation. Reductive dechlorination is the main photoreaction of PCB's in solvents such as hexane, (CROSBY and HAMADMAD, 1971). In more hydroxylic solvents, the rate of dechlorination is faster and 'polar' products are also formed, (CROSBY and LEITIS, 1969). The observed PCB photoproducts are all thought to arise through reaction of the same triplet excited state via dechlorination or neucleophilic substitution.

An area which has received very little attention has been the possibility of photointeraction between PCB's and suspended solids. Absorption of light by metallic oxides can induce reaction at the oxide surface with molecules in solution or gas phase. For a recent review see Photo-effects in Adsorbed Species, Faraday Discussions of the Chemical Society (London) Vol. 58, 1974. This photocatalysis is particularly pronounced for wide bandgap semiconductors such as titanium dioxide (rutile) and zinc oxide, but some degree of photocatalytic behaviour has been observed for iron oxides and beach sand, (KINNEY and IVANUSKI, 1969).

MARKHAM and LAIDLER (1963) studied the production of hydrogen peroxide by zinc oxide slurries under irradiation with 365 nm light. Organic additives had the effect of increasing the H_2O_2 yield indicating that, although they were consumed in the photoreaction, they were not reacting with this photoproduct. Instead it was reasoned that the organics reacted at the zinc oxide surface with oxidizing species produced during the irradiation. The photo-oxidation of benzene led to trace quantities of phenols, polyphenols and biphenyl but the major product, thought to be an organic peroxide, could not be isolated. Chlorobenzene also gave similar products in trace amounts along with a significant amount of chloride ion.

Since chlorobenzene appeared to be oxidized by the irradiated slurry, we hoped that chlorinated biphenyls would exhibit similar behaviour. Titanium dioxide was chosen as photocatalyst since it doesn't decompose upon irradiation as does zinc oxide.

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EXPERIMENTAL

Aqueous solutions of Aroclor 1254, 4,4'-dichlorobiphenyl, 2,2'-dichlorobiphenyl, 2-chlorobiphenyl, 3-chlorobiphenyl, 4-chlorobiphenyl and biphenyl were prepared by stirring the compounds with water, allowing the excess material to settle and decanting off the clear solution. The concentration of the solutions prepared in this manner was usually about 50 ppb. Methanol/water solutions were prepared similarly except that 50:50 methanol/water was used as solvent.

Equal volumes of solution and titanium dioxide suspension (0.5% in water) were thoroughly mixed and irradiated in a closed glass container, usually for 30 minutes. The ultraviolet light source was a BLAK-RAY B-100A ultraviolet light (Ultra-Violet Products, Inc.). The principle wavelength of the radiation emitted by this light was 365 nm.

Following irradiation, the samples were filtered through 0.45 μm membrane filter (Millipore Ltd.), and in the case of the methanol/water solutions, the methanol was evaporated from the solution using a rotary evaporator. The aqueous solutions were then extracted with various pesticide grade solvents of increasing polarity; hexane, benzene, ethyl ether and ethyl acetate. Extracts were dried, concentrated by evaporation and analysed using a gas-chromatograph (Tracor Model 550) equipped with both a flame ionization detector (FI) and a Ni^{63} electron capture detector (EC). The extracts were first analysed using the EC detector and a 1.8 m x 6 mm glass column packed with 10% OV1 on Gas chrome Q, for traces of starting material. This was followed by analysis on the following columns with a FI detector, Chromasorb 101, TENAX GC, CARBOWAX 20 TPA on Chromasorb W, and 3% OV1 on Chromasorb W, all temperature programmed from 100°C to 280°C at 5°/min.

The chloride ion analyses were carried out using a HgS/Hg_2Cl_2 electrode according to the method described by SEKERKA et al. (1975).

RESULTS AND DISCUSSION

When a 25 ppb aqueous solution of Aroclor 1254 in the presence of suspended titanium dioxide was irradiated at 365 nm for 30 min., no unreacted Aroclor could be detected in solution or adsorbed on the surface of TiO_2. The solution phase obtained by filtration was extracted with n-hexane and the extract analysed by G.C. No peaks were obtained with the electron capture detector indicating the absence of PCB's or other chlorinated products. A series of peaks was produced by GC analysis with a flame ionization detector but were too complex to identify by GC-MS. Extraction of the TiO_2 with n-hexane did not yield any absorbed products or starting material and a Raman spectroscopic examination of the irradiated TiO_2 revealed no adsorbed organics. Thus the disappearance of starting material was not due to adsorption on TiO_2.

In the hope of gaining a better understanding of the reaction by simplification of the processes involved, some individual mono- and di-chlorinated isomers were studied. Irradiations similar to that above were conducted on approximately 25 ppb aqueous solutions of 2-, 3-, and 4-chlorobiphenyl individually. There was no trace of 3- or 4-chloro isomers after irradiation but the 2-chlorobiphenyl was recovered 100% in the solution phase indicating no reaction of this compound. This pattern of reactivity is opposite to that observed for photoreactions involving the triplet excited state where the 2-position was observed to be most reactive and the 4-position almost unreactive, (RUZO *et al.*, 1974). It was found by analysis with a sensitive ion selective electrode, that chloride ion was liberated by irradiation. The amount of chloride produced was a function of irradiation for the first 15 minutes but no further increase was observed for longer times. A mass balance of the plateau value revealed that 80% of the available chlorine was now in the form of chloride ion. Dark control reactions were performed in each case and the chlorinated biphenyl could always be recovered unreacted from an unirradiated solution. There was no chloride ion produced in the controls. The irradiated solutions of monochlorobiphenyls were extracted and analysed by GC but no peaks were obtained with either FI or EC detectors. In particular, although biphenyl is a primary product from the photodechlorination of PCB's in hexane, no biphenyl could be detected in our irradiated solution. When the TiO_2 system was irradiated in the presence of biphenyl for 30 min., no reaction could be observed. Thus it appears unlikely that biphenyl is a primary product in the PCB/TiO_2 photolysis.

The dichloro isomers 2,2'- and 4,4'- behaved similar to 3- and 4- chloro isomers: both disappeared upon irradiation but not in the dark, chloride ions were liberated and neither biphenyl nor monochlorobiphenyl could be detected by GC after irradiation. In order to increase concentrations of the starting materials, all of the above irradiations were repeated in 50:50 methanol/water. The irradiation of higher concentrations from 35 to 1000 ppb required longer periods of time to complete the reaction but the results were analogous to the aqueous system in terms of reactivities and lack of identifiable products.

Previous studies of the reactivity of the triplet excited state of PCB's, (RUZO et al., 1974), have found that oxygen retards reaction and that the photoreaction proceeded efficiently in hexane. When nitrogen degassed solutions of 4,4'-dichlorobiphenyl/TiO_2 in methanol/water was irradiated, no reaction was observed indicating that the presence of oxygen is a necessity. The presence of water was also required for reaction since irradiation of solutions of 4,4'-dichloro/TiO_2 in hexane and hexane/methanol which were not degassed showed no reactivity. These results suggest that the reaction does not proceed via the triplet excited state, either by direct population or by energy transfer from excited TiO_2.

The observed oxygen dependence raised the possibility that the reaction involved a singlet oxygen intermediate. In order to examine this possibility, a polymer-base Rose Bengal was synthesized. This material has been shown to be an efficient, heterogeneous sensitizer of singlet oxygen, (SCHAAP et al., 1975). When the Rose Bengal-polymer was suspended in the methanol/water mixture containing 4,4'-dichlorobiphenyl and irradiated for 30 minutes at 365 nm, only the initial concentration of 4,4'-dichlorobiphenyl was recovered from the photolyte.

Our results suggest that the observed disappearance of chlorinated biphenyls and production of chloride ion in this system do not proceed by previously studied mechanisms of PCB photolysis. Instead we conclude the process resembles that mentioned in the introduction to occur on zinc oxide, where the organics react at the semiconductor surface with oxidizing species produced during illumination. GRAVELLE et al. (1971) studied the photo-oxidation of isobutane on titanium dioxide and demonstrated that $O_{2(ads)}^-$ was a photoproduct. Although $O_{2(ads)}^-$ was formed over the wavelength range from 290 to 575 nm, oxidation of isobutane only occurred for wavelengths <410 nm (ie. for energies greater than the TiO_2 bandgap). Since irradiation at energies greater than the bandgap energy produces valence band holes and conduction band electrons, and since $O_{2(ads)}^-$ presumably is formed by reaction of e^- in the conduction band with O_2, Gravelle and coworkers concluded that the photo-oxidation of isobutane was initiated by reaction of isobutane with valence band holes. The partially oxidized isobutane could then react with O_2^- to be further oxidized.

The identity of our photoproducts is presently under study but an extract from an irradiated solution of 4,4'-dichloro did not yield decachlorobiphenyl upon perchlorination, (ARMOUR, 1973). Thus we have demonstrated that dechlorination of PCB's can take place on illuminated semiconductor catalysts and may be a viable method of PCB degradation. Since up to 99% of the transport of PCB's in a body of water occurs on suspended solids, (MUNSON, 1975), we postulate that this type of process may be a significant pathway for environmental PCB degradation.

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