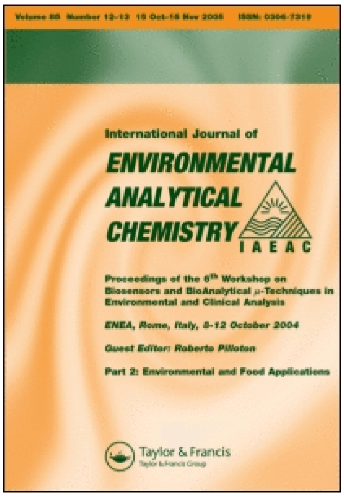

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The Photodecomposition of 1,1-Dichloro-2,2-bis(5′-chloro-2′-methoxyphenyl)ethylene (MPE), an Analogue of DDE

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The solution-phase photodecomposition of 1,1-dichloro-2,2-bis(5′-chloro-2′-methoxyphenyl)ethylene (MPE) has been studied at an excitation wavelength of 313 nm in the presence of O_2 as well as in vacuum-degassed solutions. Only two non-volatile compounds are produced: 2,5-dichloro-3-(5′-chloro-2′-methoxyphenyl)benzofuran (BFD) and a minor product which was not identified. The BFD represents approximately 90% of the total non-volatiles. The volatile products were identified as CH_3Cl, CH_4 and HCl, with CH_3Cl being approximately 99.9% of the total volatiles. Photolyses were carried out in C_6H_{12} and CCl_4 solvents, the same products being observed in both solvents. Variation of MPE concentration has little or no effect on the relative quantum yield of decomposition. The photodecomposition of MPE does not follow the same pathway as the photodecomposition of DDE.

INTRODUCTION

Many photochemical studies have been carried out on 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane (DDT).[1–3] One of the major products of photolysis of DDT is 1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene (DDE). Since DDE is a metabolite of DDT,[4] and may be produced by the action of sunlight on DDT,[5] considerable amounts of it are now found in the biosphere. However, few investigations have been made on the photochemical behaviour of DDE.[6]

We recently reported on the photodecomposition of an analogue of DDT, 1,1,1-trichloro-2,2-bis(5′-chloro-2′-methoxyphenyl)ethane (MPA).[7] One of the major products of the photolysis of MPA, in the solar spectrum ($\lambda_{cx} > 300$ nm), is an analogue of DDE, MPE. Since MPE has a large extinction coefficient in the 300-nm region ($\simeq 5.6 \times 10^3$ liter/mole-cm) it is possible that some of the other products from the photolysis of MPA arise from the secondary photolysis of MPE. This study was undertaken in order to clarify this point.

EXPERIMENTAL

Chemicals

MPE was synthesized by the alkaline dehydrochlorination of MPA using a procedure outlined in a previous publication.[7] It was purified by column chromatography (acid alumina, grade 1), eluted with dry chloroform, and finally recrystallized in absolute ethanol. The remaining traces of ethanol were removed under vacuum. The TLC and VPC examination of this product indicated a purity > 99.5%. The physical and spectroscopic properties of MPE are listed below:

white, crystalline solid, m.p. 164.5°C; infrared($ChCl_3$) 1600 cm^{-1}; n.m.r. ($CHCl_3$) ↑2.80(d of d, 2Hz,2H,-C*H*-CCl═C—), 3.21(d,8Hz,2H,═C*H*—C(OCH_3)—),3.22(d,2Hz,2H,—CCl═C*H*—),6.16(s,6H,-OCH_3); ms, M^+376 (chlorine isotope peaks indicate 4 chlorine atoms in the molecule); u.v.(C_6H_{12}) λ_{max} 295.5 nm $\varepsilon \simeq 5.6 \times 10^3$ litre/mole-cm.

Cyclohexane used for solution photolyses and u.v. spectra was fluorometric grade obtained from Harleco (60th and Woodland Ave, Philadelphia, Pa. 19143) and was used without further purification. CCl_4 was obtained from Fisher as reagent grade. VPC of both solvents showed them to be > 99% pure.

Instrumentation

Infrared spectra were recorded on a Perkin-Elmer grating infrared spectrophotometer, Model 457. U.v. spectra were determined on a Perkin-Elmer 402 u.v.-visible spectrophotometer. N.m.r. spectra were recorded on a Varian T-60 n.m.r. spectrometer; tetramethylsilane was used as an internal standard. Mass spectra were recorded using an Hitachi Perkin-Elmer RMU-6D mass spectrometer. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected.

Photochemical Procedures

The irradiating source was a 1-Kw Hanovia high-pressure Xenon-mercury lamp contained in a Schoeffel housing, air-cooled to a temperature of 110°C.

Light emitted from the lamp was passed through a 10-cm quartz cell containing distilled water in order to remove some of the infrared from the beam. The radiation was then passed through a double monochromator consisting of two 0.25-m Jarrel-Ash (Model 82-410) grating monochromators continuously flushed with N_2. The 313-nm Hg band was used for photolysis experiments, the band pass being ~ 2.5 nm. Light transmitted through the cell, at the exit slit, was measured directly with an RCA 935 phototube, the current from which was monitored on a Keithley 414A picoammeter and recorded during the entire photolysis run on a strip-chart recorder. The photolysis cell was a 1 × 4 cm high cuvette to which was attached a side-arm for degassing purposes, the cell assembly being sealed under vacuum after several freeze-thaw cycles.

Analytical Techniques

VPC was performed on a Hewlett-Packard 7620 A chromatograph equipped with a flame ionization detector. Helium was used as a carrier gas throughout. Columns used were 6′ × 0.125″ stainless steel containing silicone DC-200 (12,500 centistokes) or OV-17 on Chromosorb Q (100-120 mesh) at 10% w/w loading. Column temperature was 210°C. The injector and detector were maintained at 230°C and 255°C, respectively. Sample introduction was by a Hamilton Precision syringe through self-sealing rubber septa.

Analytical and preparative TLC was performed on Silica gel G (Merck) on microscope slides or 20 × 20 cm glass plates. Samples were eluted with hexane-methanol mixtures (2% methanol) at tank saturation. Samples scraped from the plates were eluted with methanol, filtered and evaporated. The residue was then dissolved in chloroform, filtered to remove silica gel, followed by $CHCl_3$ evaporation prior to spectral analysis. Volatile samples were sealed in glass ampoules for VPC analysis and expanded into a 10-cm infrared cell, with KBr windows, for spectral analysis.

RESULTS AND DISCUSSION

The absorption spectrum of MPE (Figure 1) is very similar to that of MPA[7] and shows that MPE exhibits considerable absorption at wavelengths > 300 nm. The major products in the photolysis of MPE in degassed solutions are BFD and CH_3Cl; traces of HCl, CH_4 and a non-volatile unidentified product were also observed. The BFD and CH_3Cl were identified from the following physical and spectral properties: BFD: white crystalline solid, m.p. 115–116°C; ms, M^+ 326 (chlorine isotope peaks indicate 3 chlorine

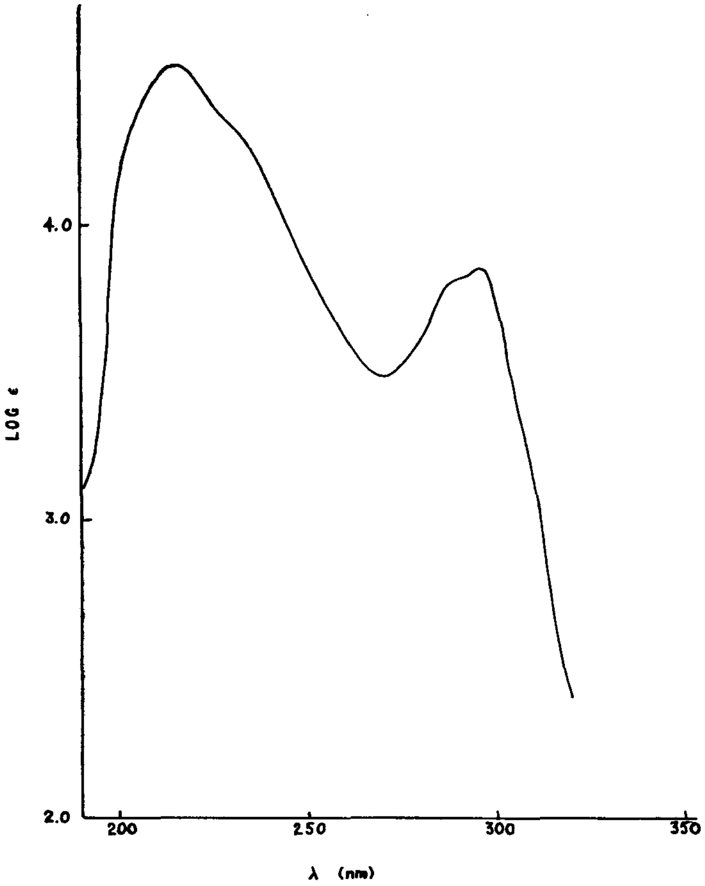

FIGURE 1 Absorption spectrum of MPE (C_6H_{12} solvent).

atoms in the molecule); n.m.r.($CDCl_3$) aromatic protons (unresolved) ↑ 2.54–3.12 (6H), 6.19 (s,3H,-OCH_3); u.v.(C_6H_{12}) λ_{max} 214, 258.5, 277.5, 287.0, 294.5 nm; CH_3Cl: analysed by peak matching techniques on VPC against authentic samples of the compound. ms, M^+ 50, 52 in ratio 3:1 respectively, peak also at mass 15; infrared (vapour) (C—H) ν 1455 cm^{-1}(s) 1355 cm^{-1}, 1015 cm^{-1}, 731 cm^{-1}. The minor non-volatile product was observed only in prolonged photolysis runs and VPC analysis showed that its yield was 1/9 that of BFD. This product was bright yellow in colour and VPC indicated that it had a lower molecular weight than BFD. The reaction may be represented as

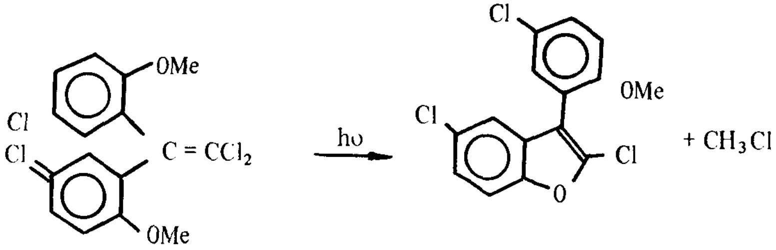

Table I summarizes the photolysis products and relative quantum yields of decomposition of MPE under various conditions. The presence of dissolved O_2 does not have any effect on the production of BFD and CH_3Cl, which suggests that the cyclization reaction occurs from a singlet state. Inspection of the data in Table I shows that, within experimental error, there appears to be no self-quenching, indicating that the reaction proceeds from a short-lived excited state. Since singlet states usually have much shorter lifetimes than triplet states this also supports the argument that the reaction likely occurs from a singlet state.

Molecular photo-elimination reactions are known to occur in chlorinated hydrocarbons[8,9] and in chlorinated ethylenes;[10] since MPE may be regarded as a disubstituted 1,1-dichloroethylene it is possible that the photolysis of MPE proceeds via a concerted mechanism and that CH_3Cl is produced by a

TABLE I

Products and relative quantum yields of the photolysis of MPE

Solvent	Irridation time (hr)	Concentration (moles/litre)	O_2 or degassed	Products	ϕ Rel. decomp.
C_6H_{12}	4	4.35×10^{-3}	degassed	BFD + CH_3Cl + unidentified non-volatile + traces CH_4 and HCl	1.00 ± 0.11
C_6H_{12}	4	3.48×10^{-3}	degassed		0.98 ± 0.11
C_6H_{12}	4	3.05×10^{-3}	degassed		0.96 ± 0.11
C_6H_{12}	4	2.61×10^{-3}	degassed		0.89 ± 0.11
C_6H_{12}	4	2.18×10^{-3}	degassed		0.80 ± 0.12
C_6H_{12}	4	1.74×10^{-3}	degassed		0.82 ± 0.12
C_6H_{12}	4	1.31×10^{-3}	degassed		0.79 ± 0.12
C_6H_{12}	4	0.87×10^{-3}	degassed		0.80 ± 0.18
C_6H_{12}	8	$\sim 10^{-3}$	degassed		—
CCl_4	8	$\sim 10^{-3}$	degassed		—
C_6H_{12}	12	$\sim 10^{-3}$	O_2	BFD + CH_3Cl + minor product + trace amounts of other volatiles and non-volatiles.	—
CCl_4	12	$\sim 10^{-3}$	O_2		—
					—

molecular elimination process. This contention is supported by the similarity of products obtained in both C_6H_{12} and CCl_4 solvents (see Table I) and by the fact that there are only two major products observed, whereas radical reactions usually produce a large number of products.

Several other points are worth noting: the products of MPE photolysis do not bear any resemblance to the products of DDE photolysis[6] or similar chlorinated compounds;[11] secondary photolysis of MPE is not responsible for the products observed in MPA photolysis.[7]

Although our results do not permit any discussion of the mechanism of this cyclisation, it is interesting to note that a simple Hückel calculation on MPE shows that the O—CH_3 bond is the weakest in the molecule, correlating well with possible carbon-oxygen bond cleavage and hence the formation of BFD.

Acknowledgements

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