

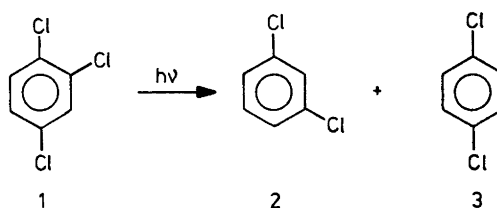
Photochemical Dechlorination of 1,2,4-Trichlorobenzene

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The photochemical dechlorination of 1,2,4-trichlorobenzene in cyclohexane and 2-propanol has been investigated. The primary products formed are 1,3- and 1,4-dichlorobenzene. The product ratio is significantly different on direct irradiation and on acetone sensitization indicating that two different reactive species give rise to dechlorination. The quantum yield for the dechlorination is 0.46 in 2-propanol under aerated conditions.



Man-spread chlorinated hydrocarbons have created a difficult environmental problem due to their persistence under natural conditions. Since these hydrocarbons are susceptible to photochemical degradation, a number of groups, including ours, have recently been studying photochemical dehalogenation of aromatic hydrocarbons. These studies show that, *e.g.*, PCB analogues may indeed be dehalogenated by photolysis, but many of these investigations have dealt with complex mixtures, making a determination of quantum efficiency and mechanism difficult.^{1–4} In some recent publications a more detailed treatment has been given.^{5–7} This prompts us to report our results on the dechlorination of 1,2,4-trichlorobenzene (*1*). These results support some of the conclusions of previous studies, but also add some new aspects.

RESULTS AND DISCUSSION

Light in the 300 nm range was used to simulate natural conditions.* Dechlorination

takes place both on direct irradiation and on sensitization with a high energy sensitizer, *e.g.*, acetone and leads mainly to a mixture of 1,3- and 1,4-dichlorobenzene but the product distribution varies substantially depending on the reaction conditions. Only traces of 1,2-dichlorobenzene were detected. The 1,3:1,4-product ratio ranges from 0.15 on direct irradiation of aerated solutions in 2-propanol or cyclohexane, to 4.8 on acetone sensitization in oxygen-free cyclohexane (Table 1).

The fate of the chlorine lost and the hydrogen donor is of mechanistic and practical interest since the formation of chlorinated secondary

Table 1. Relative yields of dichlorobenzenes in the photochemical monodehalogenation of compound *1* on direct irradiation and acetone sensitization.

Conditions	1,3:1,4-Dichlorobenzene ratio	
	Direct	Acetone sensitized
Oxygen-free 2-propanol	0.65	3.1
Aerated 2-propanol	0.15	
Oxygen-free cyclohexane	1.51	4.8
Aerated cyclohexane	0.15	

* Irradiations at 254 nm showed that the same products were formed at shorter wavelengths.

products in nature is undesirable. Irradiation in 2-propanol gave in addition to dichlorobenzenes, hydrochloric acid and acetone as the only products. Under rigorously oxygen-free conditions, a small amount of pinacol was also formed. In aerated cyclohexane solution, the major products were hydrochloric acid, cyclohexanol and cyclohexanone. No chlorocyclohexane but traces of bicyclohexyl could be detected. Under oxygen-free conditions hydrochloric acid, substantial amounts of bicyclohexyl and some chlorocyclohexane were formed. Cyclohexene is probably also formed by disproportionation of cyclohexyl radicals.

Acetone sensitization in the absence of oxygen led to increased pinacol formation in 2-propanol and increased formation of bicyclohexyl in cyclohexane. In cyclohexane some 2-cyclohexyl-2-propanol was formed. The quantitative evaluation of these results in relation to the sensitized photolysis of 1,2,4-trichlorobenzene is difficult, since the same products are formed on irradiation of acetone itself in the absence of trichlorobenzene.

The acetone-sensitized reaction should go *via* the triplet.* If the dechlorination were of triplet origin only as has been suggested for chlorobiphenyls,^{7,8} direct irradiation and sensitization should yield identical product patterns, which is not the case. Furthermore, the reaction rate but not the product pattern should be influenced by oxygen, which is a very efficient triplet quencher. The fact that a non-quenchable reaction persists on direct irradiation of continuously aerated solutions and that the product ratio is significantly different from that observed in the triplet case, implies that both the singlet and triplet-excited states of 1,2,4-trichlorobenzene lead to dechlorination in a hydrogen-donating solvent. The low 1,3:1,4 ratio (0.15) obtained in aerated solution is evidently characteristic of the singlet reaction while the high ratio (4.8) obtained on sensitization is characteristic of the triplet reaction. On direct irradiation of air-free solutions in cyclohexane

and 2-propanol, intermediate ratios of 1.5 and 0.65 were obtained (Table 1), indicating that dehalogenation from the two states occur at comparable rates. The presence of a hydrogen donor is essential as indicated by the fact that little photochemical degradation of 1,2,4-trichlorobenzene takes place in 1,1,2-trichlorotrifluoroethane solution.*

The existence of concurrent intermolecular triplet and singlet reactions of comparable efficiencies is fairly unusual in the liquid state. (For a discussion of alkanone singlet and triplet hydrogen abstraction, see Ref. 9). The relative rates of singlet and triplet reactions are slightly dependent on the solvent as shown by the lower 1,3:1,4 ratio obtained in 2-propanol (0.65) than in cyclohexane (1.5).

An interesting question is whether π -chlorine derivatives are formed in the photolysis of 1,2,4-trichlorobenzene as suggested by Lemal for chlorobenzene.⁵ The main argument for π -complex formation in the latter case is that photolysis in cyclohexane solution yields benzene and chlorocyclohexane and no phenylcyclohexane in spite of the fact that free chlorine atoms should be more efficient hydrogen abstractors than phenyl radicals by about four powers of ten.⁵ Chlorocyclohexane was formed even in the presence of oxygen, which further supports the existence of π -chlorobenzene species. In the photolysis of 1,2,4-trichlorobenzene under similar conditions, the formation of chlorocyclohexane is completely inhibited by oxygen. However, under oxygen-free conditions, chlorocyclohexane is formed from the trichlorobenzene, indicating that a complex is formed also in this case. This complex must be weaker than π -chlorobenzene since the formation of chlorocyclohexane is quenched by oxygen.

In order to get an estimate of efficiency of the photodehalogenation of 1,2,4-trichlorobenzene, the quantum yield was determined for the non-quenchable part of the reaction by direct irradiation in 2-propanol in the presence of oxygen. The quantum yields were 0.46 for the consumption of 1,2,4-trichlorobenzene, 0.38 for

* At high acceptor concentrations singlet energy transfer can occur from acetone on account of relatively slow intersystem crossing. To ensure that no singlet sensitization was taking place, the concentration of 1,2,4-trichlorobenzene was varied over two powers of ten (0.15–0.0015 M) which did not change product ratio appreciably.

* 1,2,4-Trichlorobenzene was quantitatively recovered after irradiation in 1,1,2-trichlorotrifluoroethane solution under conditions which led to approximately 30 % dehalogenation when 2-propanol was used as solvent.

formation of 1,4-dichlorobenzene and 0.06 for formation of 1,3-dichlorobenzene. These values are considerably higher than those observed for tetrachlorobiphenyls⁷ but of the same order as that determined for chlorobenzene by Lemal and co-workers.⁵

The identification of a highly efficient singlet path for dehalogenation of polychlorinated aromatic compounds is of interest also in relation to their destruction in nature. The decomposition of trichlorobenzene *via* the triplet is inhibited even by acetophenone and it is reasonable to assume that a number of efficient quenchers, including oxygen, are available in nature. Furthermore, the increased efficiency of the singlet pathway when a good hydrogen donor is present, can perhaps be utilized to increase destruction of halogenated aromatics even under natural conditions.

EXPERIMENTAL

Photochemical procedure. All irradiations were made in Pyrex glass tubing with a wall thickness of 1 mm (cut-off at 285 nm) in a Rayonette photochemical reactor fitted with a total of 16 RPR 3000 Å and RPR 3100 Å fluorescent lamps. Deaeration was effected by purging the solution with nitrogen purified by passage through a 3.5 × 50 cm tower of BASF R3-11 copper catalyst maintained at 90 °C followed by a 2 × 25 cm tower of 4 Å molecular sieves >30 min prior to and during irradiation. The nitrogen was introduced at the bottom of the reaction tube by Intramedic PE 60 polyethylene tubing *via* a rubber septum equipped with a narrow syringe needle as a gas outlet. Alternatively deaeration was carried out by three freeze-thaw cycles, namely evacuation of the solution at -80 °C, followed by equilibration at atmospheric pressure under purified nitrogen. The samples were then irradiated in a stoppered tube. Aeration was accomplished with the aid of an aquarium pump. Standard samples were prepared by diluting 50 µl (0.072 g, 0.397 mmol) of commercial, redistilled 1,2,4-trichlorobenzene with solvent to 25 ml in a volumetric flask, giving a 0.0158 M solution, which was transferred to a 1 × 50 cm Pyrex tube, in which irradiation was performed. In sensitized reactions 24 ml of solvent and 1 ml of acetone were used which allowed the sensitizer to capture >99 % of the light at 300 nm.

Analytical procedure. A PYE-104 gas chromatograph with a flame ionization detector was used. Reaction mixtures in 2-propanol were analyzed at 118 °C on a 6 mm × 1.5 m glass column packed with 10 % PEG 20 M on Chromosorb W 80-100 mesh. (1,4-Dichloro-

benzene and dicyclohexyl did not separate on this column.) Reaction mixtures in cyclohexane were analysed at 105 °C on a 6 mm × 2.7 m glass column packed with a 1:9 mixture of 10 % SF and 10 % PEG 4000 on Chromosorb W 100-120 mesh. The nitrogen carrier gas flow-rate was 50 ml/min in both cases.

Peak areas were determined by the method of peak height × peak width at 0.5 of the peak height. The peak height was measured with a ruler graduated in mm and the peak width with a magnifying glass and scale with 0.1 mm divisions. Naphthalene was used as an internal standard. Solutions of the internal standard and the reaction mixture were measured out with a 100 µl SGE syringe and mixed prior to analysis. Individual response factors were determined.

Product identification. Compounds were identified by coinjection of authentic samples and by combined GC-MS analyses using an LKB 9000 mass spectrometer connected to a Hewlett-Packard model 5750 gas chromatograph fitted with 3 mm stainless steel columns. The columns employed were a 1.5 m 10 % PEG on Chromosorb W 100-120 mesh and a 7 m 1 % SF-96 on Chromosorb W 100-120 mesh. Commercial samples were used except for bicyclohexyl which was made from cyclohexylmagnesium chloride and silver bromide¹⁰ and 2-cyclohexyl-2-propanol which was made by the addition of acetone to cyclohexylmagnesium chloride.¹¹

Irradiation of 1 in 2-propanol under nitrogen. A solution of 0.072 g (0.397 mmol) of 1 in 25 ml of 2-propanol was deaerated by the freeze-thaw method and irradiated for 30 min. GC analysis on 10 % PEG gave the following results: 1,3-dichlorobenzene, 0.019 mmol, 4.7 % (4.8 min)*; 1,4-dichlorobenzene, 0.029 mmol, 7.3 % (5.5 min); pinacol, trace (6.3 min); 1,2,4-trichlorobenzene, 0.356 mmol, 89.4 % (13.4 min).

Irradiation of 1 in 2-propanol with aeration. A solution of 1 (0.072 g) in 25 ml of 2-propanol was aerated during irradiation and irradiated for 70 min. GC analysis gave the following results: 1,3-dichlorobenzene, 0.008 mmol, 2.0 %; 1,4-dichlorobenzene, 0.061 mmol, 15.4 %; 1,2,4-trichlorobenzene, 0.322 mmol, 81.1 %.

Irradiation of 1 in 2-propanol with acetone as sensitizer. A mixture of 1 (0.072 g) and 1 ml of acetone was diluted to 25 ml with 2-propanol deaerated with a stream of nitrogen and was irradiated for 34 min. GC analysis gave the following results: 1,3-dichlorobenzene, 0.080 mmol, 20.4 %; 1,4-dichlorobenzene, 0.025 mmol, 6.2 %; pinacol, 0.034 mmol; 1,2,4-trichlorobenzene, 0.292 mmol, 74.1 %.

Irradiation of 1 in cyclohexane under nitrogen. A solution of 1 (0.072 g) in 25 ml of cyclohexane was deaerated by the freeze-thaw method and irradiated for 33 min. GC analysis on the 1:9 SF, PEG 4000 column gave the following

* Percentage based on initial starting material.

results: chlorocyclohexane, 0.004 mmol; 1,3-dichlorobenzene, 0.025 mmol, 6.4 %; 1,4-dichlorobenzene, 0.017 mmol, 4.3 %; bicyclohexyl, 0.013 mmol; 1,2,4-trichlorobenzene, 0.353 mmol, 89.8 %.

Irradiation of 1 in cyclohexane with aeration. A solution of 1 (0.076 mg, 0.418 mmol) in 25 ml of cyclohexane was aerated with a stream of air-bubbles from the bottom of the tube during irradiation for 60 min. Analysis on the 1:9 SF, PEG 4000 column gave the following results: cyclohexanone, 0.028 mmol (9.2 min); cyclohexanol, 0.036 mmol (13.6 min); 1,3-dichlorobenzene, 0.004 mmol, 0.8 % (15.6 min); 1,4-dichlorobenzene, 0.025 mmol, 5.7 % (17.5 min); 1,2,4-trichlorobenzene, 0.409 mmol, 93.3 % (44.6 min).

Irradiation of 1 in cyclohexane with acetone as sensitizer. A mixture of 1 (0.072 g) and 1 ml of acetone was diluted to 25 ml with cyclohexane, deaerated with a stream of nitrogen and irradiated for 30 min. GC analysis gave the following results: chlorocyclohexane, 0.008 mmol; 1,3-dichlorobenzene, 0.063 mmol, 15.9 %; 1,4-dichlorobenzene, 0.013 mmol, 3.8 %; 2-cyclohexyl-2-propanol, 0.022 mmol; bicyclohexyl, 0.040 mmol; 1,2,4-trichlorobenzene, 0.310 mmol, 78.2 %.

Quantum yield apparatus. The quantum yield determination was carried out using a "Black Box" apparatus as described by Zimmermann.¹² As a slight modification the reflector was machined into the shape of a nose-cone and a hole was drilled from the side to fit a PEK SEB side-mounted cooling assembly. A PEK AH-6-1-B lamp was used as the light source. The light output and the light absorbed by the photolysis mixture were determined in the following way as described by Zimmermann:¹² A quartz plate beam splitter was placed at 45° angle between the filter cell and the double compartment photolysis cell to reflect a fraction of the light into a small side cell. The splitting ratio for the specific filter combination used was determined by filling potassium ferrioxalate in the side cell and in both compartments of the photolysis cell. The amount of light absorbed by each cell was determined by the standard procedure of Hatchard and Parker.¹³ During irradiation of the reaction mixture, the side cell and the back cell of the photolysis cell were filled with potassium ferrioxalate. The amount of light absorbed by the reaction mixture was then determined by subtraction of the light transmitted to the back cell from the total amount as calculated from the splitting ratio and the amount absorbed in the side cell. The use of a double compartment cell is important, since it may otherwise be difficult to quantitatively determine the light transmitted by the photolysis mixture, resulting in calculated quantum yields which are too low.

Filter solutions. A triple compartment filter cell was used. Cell 1 was filled with 2 M nickel(II)

sulfate in 5 % sulfuric acid, cell 2 with 1 M cobalt(II) sulfate in 5 % sulfuric acid, and cell 3 with 0.0012 M bismuth(III) chloride in 14 % hydrochloric acid. This combination was opaque below 260 nm and above 300 nm and showed a maximum transmittance at 280 nm.

Quantum yield irradiations. 2-Propanol was distilled through a 30 cm Widmer column and checked for UV transparency in the region used for irradiation. A solution of 1 g of 1,2,4-trichlorobenzene in 750 ml of 2-propanol was mechanically stirred and 125 ml/min of air was pumped through the solution during irradiation. Photolyses were run to 4–5 % conversion and less than 4 % of the light was transmitted to the back cell.

Run 1. Compound 1 (1.05 g, 5.80 mmol) captured 0.66 mE of light. GC analysis gave: compound 1 consumed, 0.31 mmol, $\Phi=0.47$; 1,3-dichlorobenzene formed, 0.4 mmol, $\Phi=0.06$; 1,4-dichlorobenzene formed, 0.24 mmol, $\Phi=0.36$.

Run 2. Compound 1 (1.06 g, 5.86 mmol) captured 0.57 mE of light. GC analysis gave: compound 1 consumed, 0.25 mmol, $\Phi=0.44$; 1,3-dichlorobenzene formed, 0.03 mmol, $\Phi=0.06$; 1,4 dichlorobenzene formed, 0.23 mmol, $\Phi=0.40$.

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