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CHAPTER 2

PHOTOCHEMISTRY OF HALOGENATED BENZENE DERIVATIVES. I. TRICHLOROBENZENES : REDUCTIVE DECHLORINATION, ISOMERIZATION AND FORMATION OF POLYCHLOROBIPHENYLS

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Summary. Irradiation of the three trichlorobenzenes with $\lambda > 285$ nm in a few solvents results in reductive dechlorination as the major reaction, and isomerization and formation of polychlorobiphenyls in some cases.

Introduction. The photochemistry of polychlorobenzenes has not received much attention until recently. Plimmer *et al.* investigated the photolysis of hexachlorobenzene in methanol at $\lambda > 260$ nm;¹ the photoproducts were penta- and tetrachlorobenzenes, formed by reductive dechlorination, together with pentachlorobenzyl alcohol. Norris *et al.* have shown that hexachlorobenzene was not photodegradable, whereas hexabromobenzene was completely degraded within 24 hrs.² Finally, neat (poly)chlorobenzenes (mono-, di-, tri- and tetrachlorobenzenes, and hexachlorobenzene) have been exposed to sunlight for 56 days by Uyeta *et al.*³ They found polychlorobiphenyls (PCB's) amongst the reaction products.

Since trichlorobenzenes are frequently found in effluents from chemical industry and sewage treatment plants⁴, in natural waters⁴⁻⁸ and in tap water⁹, their photochemistry in water at wavelengths $\lambda > 285$ nm would be of potential interest from an environmental point of view. The lowest wavelength of the solar spectrum recorded on earth is about 285 nm.¹⁰

The present report presents preliminary results on the photochemistry of the three trichlorobenzenes in methanol and a mixture of water and acetonitrile using radiation of $\lambda > 285$ nm.

Results and discussion.

The results of irradiations of deaerated methanolic solutions of 1,2,4-trichlorobenzene (1,2,4-TCB; **1**), 1,2,3-TCB (**2**) and 1,3,5-TCB (**3**) are presented in Table I (section 1). Reductive dechlorination takes place very rapidly, with **1** as the most reactive starting material. In the case of **1**, no *o*-dichlorobenzene (*o*-DCB) is found although its formation is possible. The yield of *p*-dichlorobenzene (*p*-DCB) is much higher than that of the *meta* isomer. The photoreaction of **2** and **3**, although being slower than that of **1**, yielded monochlorobenzene (MCB) in addition to dichlorobenzenes.

Quite unexpectedly, small amounts of *p*-DCB were observed among the photoproducts from both **2** and **3**. A further observation is the predominance of *m*-DCB (from **2**) or *p*-DCB (from **1**) over *o*-DCB formation, which is likely a result of relief of steric hindrance in the former case.

In Table I are listed the results of sensitization (with acetone, $E_T = 79 - 82$ kcal/mole¹¹) in section 2, and quenching experiments (with isoprene, $E_T = 60$ kcal/mole¹¹, and oxygen) in sections

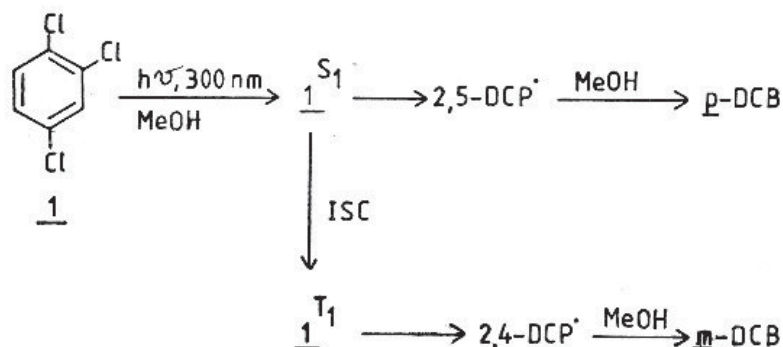
3 and 4. Both sensitization and quenching have significant effects; quenching mainly on the reaction rate (in the case of 2 and 3), and sensitization on the product distribution, which indicates that the various products are formed from different excited states. o-DCB is also formed from 1, in the presence of sensitizer, and with two of the three substrates, m-DCB is formed in higher yields upon sensitization, *e.g.* in the case of 1 there is a 26-fold increase of m-DCB formation (*cf.* Table I, section 2). Upon acetone-sensitized reaction of 3, about 8% of 2,3',4,5',6-pentachlorobiphenyl is formed (based on converted starting material) along with traces of tetrachlorobiphenyls and three other, unidentified, products. The PCB formation is in line with the findings of Uyeta *et al.*³ and clearly results from a coupling of 3,5-dichlorophenyl radicals with starting compound. In the reactions with isoprene as quencher, a product is formed, which might originate from the diene structure, as complete absence of chlorine atoms was observed with this product.

The last section of Table I shows the results of photoreactions of 1 - 3 in water with acetonitrile as a cosolvent, which solubilizes the organic substrate. In this medium reactions are slowed down significantly, and again unexpectedly, the isomerization product 1 is formed from both 2 and 3. Photolysis of m-DCB in water-acetonitrile did not afford any isomerization product (o- or p-DCB), which clearly shows that in this case p-DCB is formed *via* 1 in the photoreactions of 2 and 3.

Only with compound 3, a number of PCB's has been identified. Chlorophenols were not among the reaction products in this (aqueous) medium.

In Scheme 1 an outline is given for the course of events after excitation of 1. p-DCB is formed from singlet excited 1, whereas m-DCB originates from the triplet excited state after intersystem crossing from singlet excited 1. However, acetone-sensitization of 1 does also account for the formation of substantial amounts of p-DCB, which clearly cannot be explained by the presented Scheme. Direct photolysis of 1 could have led to p-DCB, but this has to be ruled out by the fact that the sensitizer absorbed nearly all of the radiation available. A plausible explanation would then be a reaction occurring from both singlet and triplet excited state leading to p-DCB.

On the other hand, the quenching experiments with 1 support the mechanism outlined in Scheme 1; the major product is then p-DCB and there are only minute amounts of m-DCB. By contrast, m-DCB



Scheme 1

Table I. Photoreactions of trichlorobenzenes (TCB's)

| Substrate | Substrate concn. ($10^{-3}M$) | Irradn. time (hr) | Substrate disappearance (%) | Reductive dechlorination products (%) ^a | Other photoproducts |
|--|---------------------------------|-------------------|-----------------------------|--|--|
| 1. IN DEAERATED METHANOL ^b | | | | | |
| 1 | 6.12 | 7 | 79.3 | <u>m</u> -DCB(1.9), <u>p</u> -DCB(73.4) | - |
| 2 | 5.56 | 22 | 67.6 | <u>o</u> -DCB(13.3), <u>m</u> -DCB(72.3), MCB(8.0) | <u>p</u> -DCB(1.3) |
| 3 | 5.40 | 22 | 50.7 | <u>m</u> -DCB(70.4), MCB(5.5) | <u>p</u> -DCB(1.7) |
| 2. IN DEAERATED METHANOL + ACETONE ($5.53 \times 10^{-1}M$) | | | | | |
| 1 | 5.07 | 5 | 53.5 | <u>o</u> -DCB(1.6), <u>m</u> -DCB(52.8), <u>p</u> -DCB(25.8), MCB(0.6) | - |
| 2 | 5.18 | 1.5 | 24.7 | <u>o</u> -DCB(7.6), <u>m</u> -DCB(91.4) | - |
| 3 | 5.23 | 3 | 72.3 | <u>m</u> -DCB(37.0), MCB(2.9) | 2,3',4,5',6-pentachlorobiphenyl(8) ^c + tetrachlorobiphenyls + 3 unidentified products |
| 3. IN DEAERATED METHANOL + ISOPRENE ($8.71 \times 10^{-3}M$) | | | | | |
| 1 | 6.17 | 7 | 84.9 | <u>m</u> -DCB(1.6), <u>p</u> -DCB(80.7) | - |
| 2 | 5.67 | 22 | 56.6 | <u>o</u> -DCB(12.1), <u>m</u> -DCB(64.8) | d |
| 3 | 5.40 | 22 | 38.7 | <u>m</u> -DCB(67.9) | d |
| 4. IN OXYGENATED METHANOL ^e | | | | | |
| 1 | 5.29 | 7 | 96.2 | <u>m</u> -DCB(1.6), <u>p</u> -DCB(72.3) | - |
| 2 | 5.73 | 22 | 63.0 | <u>o</u> -DCB(12.7), <u>m</u> -DCB(70.6), MCB(5.3) | <u>p</u> -DCB(2.1) |
| 3 | 5.73 | 22 | 30.5 | <u>m</u> -DCB(90.3) | <u>o</u> -DCB(3.6), <u>p</u> -DCB(2.1) |
| 5. IN A WATER-ACETONITRILE MIXTURE ^f | | | | | |
| 1 | 6.67 | 51 | 39.9 | <u>o</u> -DCB(<1), <u>m</u> -DCB(1.9), <u>p</u> -DCB(51.5) | - |
| 2 | 5.51 | 51 | 27.8 | <u>o</u> -DCB(9.8), <u>m</u> -DCB(22.9) | 1(8.5), <u>p</u> -DCB(4.9) |
| 3 | 5.29 | 51 | 38.6 | <u>m</u> -DCB(22.5) | 1(8.8), 2(<1), <u>p</u> -DCB(1.9), 2,3',4,5',6-pentachlorobiphenyl(~4) ^c + penta- + tetrachlorobiphenyls (<1) |

a. Percentages shown in parentheses represent chemical yields which were calculated from the amount of disappeared starting material.

b. Nitrogen was flushed through the solution for two hours prior to the irradiation.

c. Calculated relative to the amount of m-DCB (photoproduct) used as an internal standard.

d. This product could not be identified.

e. Air was bubbled through the solution for two hours.

f. One to one by volume.

is the major product upon irradiation of 2 and 3, both in the presence and in the absence of quencher. In these cases, both m-DCB and o-DCB (in the case of 2) are possibly formed from the singlet excited state.

Of special interest are the photo-isomerization reactions (with 2 and 3) and the formation of PCB (with 3). To our knowledge the rearrangement of chlorine atoms on a phenyl ring has never been described before in solution phase using "low energy" radiation (*i.e.* with $\lambda > 285$ nm). For this isomerization reaction there are, in principle, at least two possible mechanisms which should be considered: 1. rearrangement of the benzene nucleus resulting in isomeric intermediates (*e.g.* benzvalene) which may revert to isomerized products, and 2. protonation-deprotonation with intermediate occurrence of a chlorine shift to form the isomerized products. The first mechanism is well-known¹², but seems to be related to the use of proper radiation (254 nm). The second mechanism might be more attractive under the conditions of the experiments chosen in this study. Further study will be required to differentiate between the mechanistic pathways available for this novel type of photo-isomerization of trichlorobenzenes.

With regard to the formation of PCB our observations are the first examples of this type of reaction in solution phase. Apparently, the 3,5-dichlorophenyl radicals are stable enough to "survive", at least in part, hydrogen donation by methanol. The other dichlorophenyl radicals apparently are not, because only dichlorobenzenes are observed in these cases. Eventually, the 3,5-dichlorophenyl radicals end up in part as chlorobiphenyls after addition to ground state molecules of 3.

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SUPPLEMENT TO CHAPTER 2EXPERIMENTAL SECTION

Substrate. 1,2,4-Trichlorobenzene (1) was provided by Koninklijke Shell Laboratories, Amsterdam. 1,2,3- and 1,3,5-Trichlorobenzene (2,3) were obtained from Aldrich Chemical Co., Inc., Milwaukee, Wis.

Solvents. Sources of solvents are described in Chapter 4.

Quencher. Isoprime was used from the kit bought from J.T. Baker Chemical Co.

Standards. o-, m-, p-Dichlorobenzenes and monochlorobenzene were available in the kit of standards supplied by Chem. Service, Inc., West Chester. 2,3',4,5',6-Pentachlorobiphenyl was synthesized by a coupling reaction between 1,3,5-trichlorobenzene and 3,5-dichloroaniline.

Irradiations. Sample solutions were irradiated in the photoreactor mentioned in e.g. Chapter 4; the flux density being ca. 0.525 milliwatts/cm². The substrate 2 in degassed methanol in the presence of acetone (0.553M) was irradiated for 1.5 hours; the purpose ^{was} to have minimum error for calculations of the yields of the desired products which could be disturbed by photoproducts of acetone. The time of photoreaction, in all other experiments was arbitrarily chosen.

Gas Chromatography. This was carried out on a Hewlett-Packard 5830A instrument with a flame ionization detector with a 18850 GC terminal. Gas chromatograph was equipped with glass column (2m X 0.2 cm) containing 3% Carbowax 20M on 140-160 mesh Chromosorb WAW. Initial temperature of the oven was 80°C with the exception of the analysis of photolyzate of substrate 3 in methanol containing acetone, in which case the initial

temperature was 130°C; the aim being to separate the peaks due to 3 and some photoproducts (probably originating from acetone). The initial oven temperature was kept constant for 2 min after injection, whereafter the oven was programmed to 240°C at a rate of 8°C/min. Carrier gas (He) was 27 ml/min. Injection port temperature was 250°C and detector temperature 300°C. The samples photolysed in a H₂O:CH₃CN mixture were directly injected onto GC for quantifications. No apparent destruction of the column by water injection was observed. The identification of the photoproducts, by comparison of retention times (in addition to mass spectrometry) with ^{those} of reference compounds, were also performed on this column.

Combined Gas Chromatography-Mass Spectrometry. This was conducted on a Hewlett-Packard 5984A unit operating in the electron-impact mode at 70 eV. The glass column (2m X 2mm) was packed with 0.2% Carbowax 20M on 100-120 mesh Chromosorb W. The other conditions were as mentioned above; the initial temperature being 80°C.

Identification of Photoproducts. The photoproducts were identified by comparing their retention times and mass spectra with those of standard compounds. The samples containing water were treated with CH₂Cl₂ and the organic layers were injected onto GC-MS unit. In order to find whether chlorophenols are produced, the CH₂Cl₂ extracts of such samples after treating with diazomethane (CH₂N₂) were also injected to GC-MS; the results being negative.