

Dioxin '97, Indianapolis, Indiana, USA

Reaction of 2,3,3',4,4',6 Hexachlorobiphenyl (PCB 158) with Calciumoxide in aqueous solution?

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Abstract

The experiments showed the decline of PCB 158 in aqueous Ca(OH)₂ solution. However, the expected acetylated phenol peak of the degradation product did not appear in the chromatograms. So we conclude that the nucleophilic substitution of PCB 158 by hydroxide ions does not lead just to mono-hydroxy biphenyls.

Introduction

Aromatic compounds containing electron-withdrawing substituents, e.g. Chlorine, can undergo nucleophilic substitution reactions¹⁾. These reactions proceed the better, the more of these substituents are present. While the preparation of phenol from chlorobenzene (Dow-Process) needs drastic conditions, hexachlorobenzene already reacts in aqueous sodium hydroxide solution at temperatures between 100° and 200° C²⁻⁴⁾. Thus it is no wonder that in 1983 Brunell and Singleton reported the reaction of polychlorinated biphenyls (PCB) with polyethylenglycol (PEG) and potassiumhydroxide for the decontamination of transformer oil⁵⁾. This chemical dechlorination is now a widely recognized alternative to thermal treatment of chlorinated aromatic hydrocarbons⁶⁾. Because of the low water solubility⁷⁾ the reaction seemed to be restricted to non-polar media. From PEG and potassium hydroxide the corresponding alkoxide is formed which conducts the nucleophilic attack on the halogenated aromatic compound. At temperatures between 75° C and 200° C the conversion took place in 10 to 120 minutes. The degradation rates were good, and the PCB-O-PEG-ether could be isolated as the reaction products. Similar in principle are the reactions of PCB with PEG/sodiumhydroxide or the use of thiolate nucleophiles^{8,9)}.

Experiments to decontaminate soils using PEG/KOH were successful on spiked sand and on native soils with less than 2% water content. However, rates decreased strongly with rising amount of water in the soil samples¹⁰⁾. Excavated soils can be treated similarly at temperatures between 100° C and 200° C. This procedure, however, destroys soil texture and its microflora¹¹⁾.

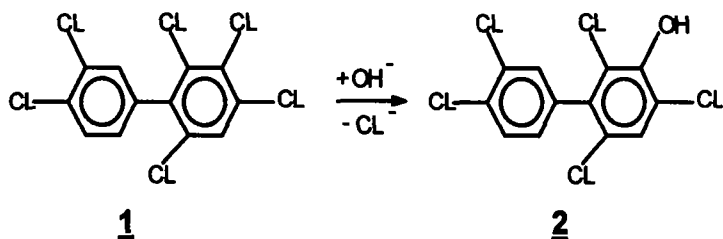
An Australian paper of 1994 reported the nearly quantitative degradation of halogenated aromatic hydrocarbons by grinding the contaminated matrices with Calciumoxide in a ball mill¹²⁾. The results were not discussed, but at least for the more volatile substances evaporation from the matrices may be probable because of the high temperatures caused by the grinding process; but in analogy to the

reaction of e.g. PEG/KOH with PCB a nucleophilic substitution of chlorine by hydroxide ions from Calciumhydroxide may be possible as well.

Using $\text{CaO}/\text{Ca}(\text{OH})_2$ for the decontamination of PCB contaminated soils would have the advantage that the excess reagent could be neutralized with CO_2 to result CaCO_3 , a natural soil component. Moreover, modified CaO had already been used to immobilize PCB in soil¹³.

We decided to investigate the nucleophilic substitution of chlorine in PCB by hydroxide using a simple experiment. A single PCB isomer (PCB 158) was adsorbed on the wall of a reaction flask, which then was filled with an aqueous solution of $\text{Ca}(\text{OH})_2$. According to its (low) solubility some of the PCB will be solved and should react with the hydroxide ions. Analysing the time depending concentration shift of the PCB should indicate whether a reaction takes place. It can, however, not be excluded that the nucleophil reacts with the sorbed molecule. The experimental curve would show the overall degradation rate. If a reaction takes place, the product supposed should be extracted from the aqueous solution after derivatisation and be quantified as well.

We used 2,3,3',4,4',6-Hexachlorobiphenyl (PCB 158) **1** as an example because of being not coplanar and the supposed reaction will not easily lead to the corresponding polychlorinated dibenzofuran (PCDF) in a subsequent reaction.



Experimental Methods

Resigrade solvents used were purchased from Baker, the CaO p.a. from Merck and 2,3,3',4,4',6-hexachlorobiphenyl (PCB 158) and 2,3,3',4,5'-pentachloro-4'-hydroxybiphenyl (RPM 21) from Promochem. Water had Serapur quality.

A solution of 50 $\mu\text{g}/\text{ml}$ of PCB 158 in hexane was prepared. 100 μl of this solution were given into a 10 ml round flask with a magnetic stir-stick and the solvent was evaporated at 200 mbar and 40 $^\circ\text{C}$ (about 15 minutes) or blown off by nitrogen. 5 ml of a saturated $\text{Ca}(\text{OH})_2$ solution (pH 12,6) were added, the flask was closed and placed in a heated oil bath (65 $^\circ\text{C} \pm 2$ $^\circ\text{C}$; 85 $^\circ\text{C} \pm 2$ $^\circ\text{C}$) with vigorous stirring for a certain time. After different times two flasks were allowed to cool to room temperature in each case and neutralized with 200 μl acetanhydride for derivatization of possible phenolic products¹⁴. 1 ml Hexane was given to the aqueous phase and the mixture was shaken vigorously for 1 minute. After phase separation hexane layer was transferred into a GC vial and the amount of PCB 158 in each vial was determined twice by gas chromatography. Measurements were carried out using a HP 5890 Series II GC/ECD from Hewlett Packard with an autosampler and a split/splitless injector further equipped with a 30 m DB-5 capillary column (J&W) and a 15 m DB-1 capillary column (J&W), respectively. Carrier gas were helium (1 ml/min) and makeup gas nitrogen (60 ml/min). The temperature program started at 60 $^\circ\text{C}$ for 2 min, heated to 180 $^\circ\text{C}$ with 20 $^\circ\text{C}/\text{min}$ remained there for 2 min and heated then to the final temperature of 320 $^\circ\text{C}$ with 30 $^\circ\text{C}/\text{min}$. The final temperature was kept for 5 more minutes. Quantification of the experiments was done by calibration curves. For determination of the recovery rates, the basic $\text{Ca}(\text{OH})_2$ solution was changed to water and the flasks were heated briefly to the reaction temperature. Rates were 95 \pm 5%.

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Results and Discussion

One can see from the figure 1 that the interaction of hydroxide ions with PCB 158 leads to decreasing concentrations depending on the reaction time. The temperature effect seems of less importance. At

65° C as well as at 85° C the amounts of PCB 158 recovered is about 50% after one day and 30% after five days.

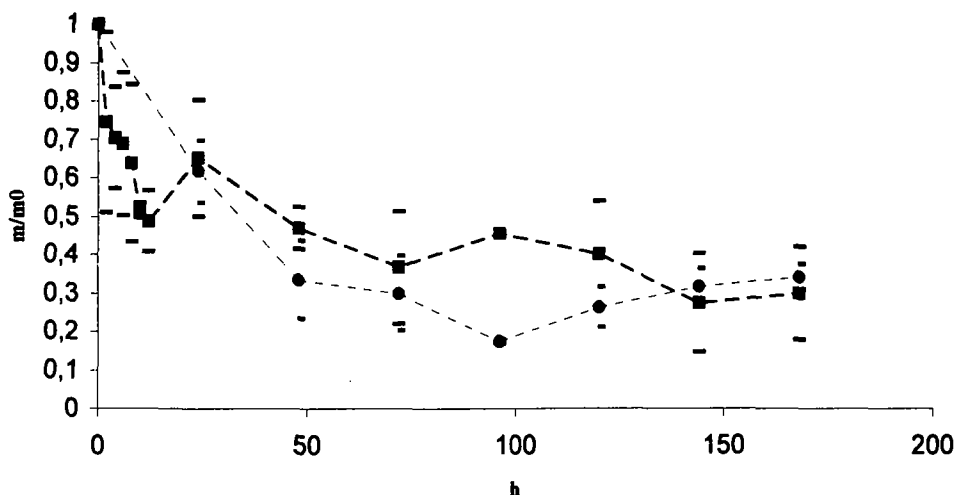


Figure 1: Decline of PCB 158 in aqueous $\text{Ca}(\text{OH})_2$ solution at $85 \pm 2^\circ\text{C}$ (■, standard deviation -) and $65 \pm 2^\circ\text{C}$ (●, standard deviation -).

However, the expected acetylated phenol peak of the degradation product did not appear in the chromatograms. To investigate this further RPM 21 was purchased as the most similar Hydroxy-PCB expected and acylated under the same experimental conditions. This substance could be very well acylated and showed a distinct gas chromatographic peak. Comparing its chromatogram with that of the degradation experiments one of the poor peaks appearing next to the educt could possibly be the reaction product but its concentration was too less to identify the molecule by mass-spectrometry.

To verify that the concentration decline of PCB 158 was not due to an evaporation from the flask the reactions were repeated in closed Wheaton Vials. The mixtures were weighted before and after the degradation procedure, in no case a loss of material could be detected. Moreover, subsequent to the extraction of the reaction mixture, the vials were extracted with acetone in a supersonic bath to solve adsorbed molecules. Measurement of the combined organic solutions showed a better correlation of concentration decline and time but the results obtained were very similar in the rates and the absolute concentrations, respectively, to the first ones. Again no phenolic degradation product could be detected.

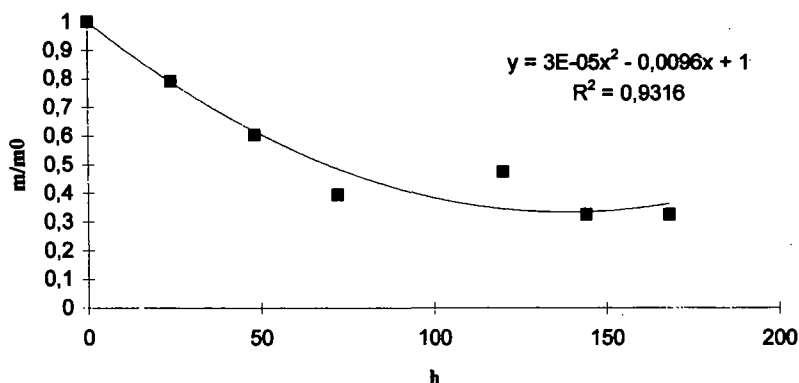


Figure 2: Decrease of the amount of PCB 158 in aqueous $\text{Ca}(\text{OH})_2$ solution at $65 \pm 2^\circ \text{C}$ in Wheaton Vials.

From the results we conclude that the nucleophilic substitution of PCB 158 does not lead just to monohydroxy biphenyls but to polyhydroxylated derivatives which may react to chinoid products as reported recently¹⁵⁾. That is why we could not find the acetylated derivatives of the expected polychlorinated biphenyls. Another explanation for the absence of the proposed degradation product may be that the primary phenol will be deprotonated to give a phenolate ion. As this is much more nucleophilic than the hydroxide ions it may dimerize with another PCB molecule or even polymerize. The resulting products e.g. decachlorodibiphenylether would not be detectable by gas chromatography. Experiments using thinlayer chromatography to detect any substitution product are under study.

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