

Activation energies of the nucleophilic substitution reaction of Decachlorobiphenyl with sodiummethanthiolate.

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Introduction

Polychlorinated biphenyls (PCB) are of persistent ubiquity in the total environment. So it takes no wonder that many methods for mineralisation or degradation have been tested in the past. Like other desactivated aromatic compounds these molecules may undergo substitution of chlorine by an appropriate nucleophil. This chemical dechlorination is now a widely recognized alternative to the thermal treatment of specific matrices poisoned with chlorinated aromatic hydrocarbons [1].

As early as 1983 Brunell and Singelton reported the reaction of polychlorinated biphenyls with polyethylenglycol (PEG) and potassiumhydroxide for the decontamination of transformer oil. 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 [2,3]. Iaconianni reported likewise in his thesis of 1983 about different substitution reactions of polyethylene glycol salts with PCB and other chlorinated aromatics [4]. Most of the experiments he described led from defined chloroaromatics to well characterized substitution products. All this experiments were, however, carried out in non-polar or dipolar/aprotic organic solvents. Experiments of Brunelle and Singleton to decontaminate soils using PEG/KOH were successful only on spiked sand and on native soils with less than 2% water content. Rates decreased strongly with rising amount of water in the soil samples [5]. Because of the low water solubility of the PCB the reaction seemed to be restricted to the non-polar media [6].

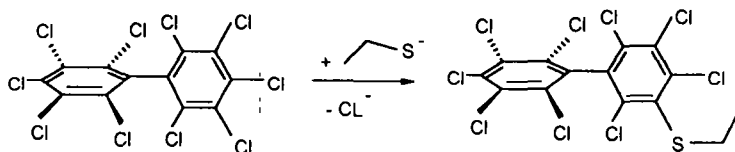
Beside those experiments some other papers were published dealing with treatment of PCB contaminated soil or sewage sludge with hydroxide ions under environmental conditions, what means in aqueous solution or in wet matrices [7-9].

In 1988 van der Valk and Dao reported about degradation of PCB in sewage sludge during alkaline saponification at 90°C ; similar experiments were carried out by Paya Perez et al. ten years later to find corresponding results. Similar to Brunell's results the first could find ethoxy derivats of the PCB 180 when spiked sludge was with treated in the laboratory with an mixture of ethanol and aqueous KOH, the latter made no attempt to name any resulting

molecules of the substitution. Only the loss of PCB concentration was measured and no reaction product was specified. In no case the authors did discuss their results with respect to the mass balance, e.g. van der Valk did not report about their recoveries of ethoxylated PCB 180. Regarding our experiment on reaction of PCB 158 with aqueous calcium hydroxide solution we suggest that they were very low.

Our attempts to form hydroxylated PCB in a substitution reaction of PCB with aqueous calcium hydroxide solution has shown the well known decline of the PCB concentration but the absence of any detectable phenolic product. We discussed possible subsequent reactions to give chinoid products or bisarylethers but at least it did not become clear whether that reaction has taken place at all [10,11]. Possibly all we have measured was the sorption of PCB at the wall of the reaction vessel or on the surface of traces of unsolved calcium hydroxide. As far as we see, none of the experiments of nucleophilic substitution reaction on PCB with aqueous alkaline solutions could doubtless prove this reaction by showing the expected phenolic derivats. Therefore, the main question remaining is whether a nucleophilic substitution reaction on PCB can be conducted in polar protic solvents at moderate temperatures in measurable times at all.

To examine this systematically, we have conducted a series of experiments using different alcoholic solvents at different temperatures in the reaction of Decachlorobiphenyl (DCB) with sodiummethanthiolate as nucleophil.



The reagent was chosen because of its pK_a which is far below that of the alcohols used. So we should not fear for competitive reactions of the corresponding alcoholates. Correlation of the k , values of the reaction rate at different temperatures with the reciprocal of the temperatures should lead in an Arrhenius plot to the activation energies of these substitutions. Using the solvent polarity parameters $E_T(30)$ of Reichardt we would try to extrapolate onto water[12].

Experimental

Methanol, ethanol, 2-propanol and 2-methyl-2-butanol were bought from Merck in SeccoSolv quality (p.a.; dried) sodiummethanthiolate was from Fluka (90%) and Decachlorobiphenyl (PCB 209, DCB) was from Promochem. Reaction rates were measured using a Hewlett Packard 5890 II GC equipped with an autosampler and computer assisted data recording. The autosampler was thermostated to the required temperatures by a Haake FE 2 thermostat.

Following the split/splitless injector gas chromatographic separation of the DCB was done on a J&W capillary column (DB 5-60N 0,23 mm ID 0,25 μ m film) with detection by an Electron-Capture-Detector (ECD). Helium was used as carrier gas and nitrogen as make-up gas. The injector temperature was 270 $^\circ$ C and the ECD temperature was 320 $^\circ$ C. The temperature program of the oven started at 100 $^\circ$ C for 1 min., then heated at 30 $^\circ$ C/min. to the final temperature of 300 $^\circ$ C that was kept for 20 min.

Quantification was done via separate calibration curves for each alcoholic solution of the substrate; all correlation coefficients were than 0.99.

The measurements were carried out in GC vials.

1 ml of a solution of 1 µg/ml DCB and 1 ml of a solution of 337,4 µg/ml sodiummethanthiolate in the respective alcohol were given into a GC vial. The solution was shaken and then was placed at once into the thermostated autosampler deck. Every 35 min. a probe from the reaction mixture was analyzed gaschromatographically for the decline of the DCB concentration. For each solvent the measurements were carried out twice and the mean values of the concentration was plotted versus the reaction time.

Concentration of DCB has to be corrected for the loss of solvent over the period of the measurements. This was done by analyzing an standard solution of the reagent in the corresponding solvent under the same conditions without any nucleophil. The time course of the rise of concentration has to be subtracted from the measured values of the reaction.

Results and discussion

The first surprising result came from the calibration. Though we used equal concentration ranges, the slopes of the curves were quite different for the different solvents. They were loosely correlatable with the dipolmoments, but not with the $E_T(30)$ -values of the alcohols. Perhaps these represent the Freundlich-Isotherms of a specific xenobiotic (DCB) to a specific surface (vial) in the presence of different dissolving liquids. Thus the activity of DCB comes out to fall from ethanol > methylbutanol > methanol > to propanol and has to be quantified separately for each series of experiments. Fortunately, initial concentrations of DCB could not get too low. As the concentration of the nucleophile was 10^3 -fold that of the PCB we have run a pseudo-first-order reactions for the substitution and because of this only the relative decline of the DCB was of any interest. From reaction kinetics we expected $m = m_0 e^{-kt}$ where m is the amount of the PCB at the time t , m_0 its starting amount and k the wanted rate constant. For m is proportional to the analyzed GC-area one could find k by plotting or calculating: $\ln(\text{area}/\text{area}_0) = -kt$ or $\ln(\text{area}_0/\text{area}) = kt$. Plotting m_0/m versus reaction time gave degradation curves with a plain exponential correlation for three of the solvents at all temperatures. Only exception was methylbutanol, for which no degradation of DCB was found at any temperature. From the slopes of the logarithmic plots one could calculate the reaction rate constants k_i of the substitution in ethanol, methanol and isopropanol at the given temperatures. One can see from their values (Tab. 1) the rise with temperature as well as an essential influence of the solvent used.

Solvens	Methanol	Ethanol	Isopropanol
Temp / °C		k_i / min^{-1}	
30	3.625×10^{-6}	2.897×10^{-5}	1.991×10^{-4}
40	6.054×10^{-6}	5.237×10^{-5}	3.756×10^{-4}
50	1.29×10^{-5}	1.125×10^{-4}	6.05×10^{-4}
60	2.733×10^{-5}	1.751×10^{-4}	(2.232×10^{-4})

Table 1: Reaction rate constants at different temperatures for the nucleophilic substitution of chlorine at DCB by ethanthiolate in different solvents.

From the Arrhenius equation $k_0 = k e^{-E_a/RT}$ one gets the activation energy E_a of the reaction by correlating $\ln k$ to $1/T$. Using the rate constants from above, the energies for the respective solvents were calculated to be methanol 57.081 kJ/mol; ethanol 51.787 kJ/mol and

isopropanol 45.315 kJ/mol. Concerning to the proposed ionic σ - complex of the reaction the results were not what one has expected. Polar transition states are usually stabilized by polar solvents and from Reichardt's tables of solvent polarity one can see that the solvents are getting more polar in the order isopropanol < ethanol < methanol. Nevertheless the correlation of the activation energies found with the $E_T(30)$ values led to a satisfying linear correlation which we extrapolated to the polarity of water (Diagram 1).

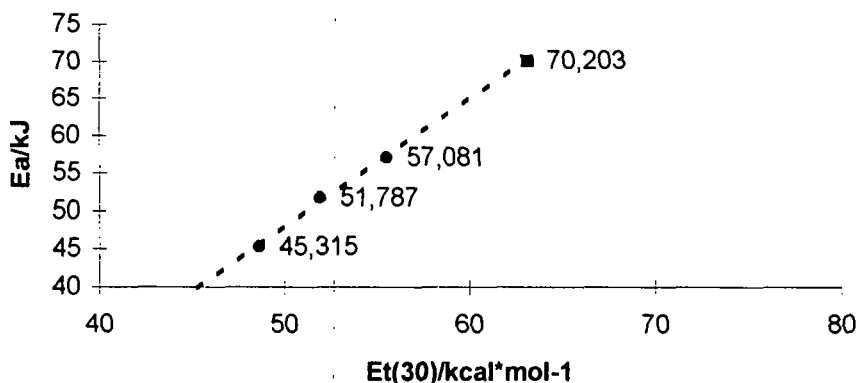


Diagram 1: Plot of the activation energies E_a of the nucleophilic substitution at DCB in different alcohols versus their polarity parameter $E_T(30)$ and extrapolation to water.

We interpret the values of the activation energies found and likewise the slope of the energy / polarity plot in the way that the measured values not solely represent the pure activation energies but also reflect the influence of the solubility of the nucleophile. If there are similar effects on the solubility of the thiolate as have been found for that of the DCB conditions for a pseudo-first-order reaction might not be given any more. Presently this question is under study beside experiments about the influence of the type of the nucleophile used.

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