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Destruction of 2,2',3 - Trichlorobiphenyl in Aqueous Solution by Hydrous Pyrolysis / Oxidation (HPO)

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Abstract

Aqueous, low-temperature oxidation rates for the polychlorinated biphenyl (PCB) congener 2,2',3-trichlorobiphenyl have been measured in aqueous phosphate-buffered solutions using Dickson-type reaction vessels. Concentrations of the target compounds were determined by gas chromatography and compound identification was verified by gas chromatography - mass spectrometry. The reaction temperatures ranged from 131°C to 165°C and the activation energy for the destruction of 2,2',3-trichlorobiphenyl was estimated to be 124 kJ/mole. In a low-concentration experiment (approximately 500 ng/g starting concentration), 2,2',3-trichlorobiphenyl concentration reached non-detect in two days at 135°C . In a much higher concentration experiment (approximately 24,000 ng/g initial loading), nearly 40% of the initial 2,2',3-trichlorobiphenyl concentration, or about 10,000 ng/g was destroyed at 161°C in 18 days. The 2,2',3-trichlorobiphenyl concentration of 24,000 ng/g measured at 131°C represents a greater than 100 fold increase in the aqueous solubility compared to the value of 200 ng/g at 20°C reported by Mackay et al. (1992). During the experiments the reacted portion of the 2,2',3-trichlorobiphenyl was completely mineralized, as indicated by a stoichiometric production of inorganic carbon and chloride ion, and no intermediates amenable to gas chromatography were observed during the HPO experiments. These preliminary experiments indicate that hydrous pyrolysis/oxidation (HPO) may be a useful alternative method for remediating soil and groundwater contaminated with PCBs.

Introduction

Polychlorinated biphenyls (PCBs) belong to a class of industrial chlorinated aromatic compounds which are known to be among the most persistent and widely distributed pollutants in the global ecosystem. Their physical and chemical stability, along with their excellent dielectric properties, led to the widespread industrial use of these compounds as capacitor dielectrics and transformer coolants, but they have also been used as platicizers, hydraulic fluids, heat exchanger fluids, lubricating oils and cutting oils (Hutzinger et al., 1974; World Health Organization, 1976). The characteristics which make PCBs industrially desirable also make them persist and accumulate in the environment. These chemicals are of concern because of their toxicity, resistance to degradation and tendency to bioaccumulate. Because of their persistence and ecological damage from soil, sediment and water pollution, their manufacture in the U.S. was discontinued in 1979.

Leaks and disposal of industrial fluids have resulted in widespread soil pollution. In addition to soil contamination by direct dumping, large quantities of PCB-containing wastes, such as transformers and capacitors, have been removed from service and treated as solid wastes. As the original containers decay, their contents are released into the surrounding soil to result in a larger environmental problem. Although the widespread migration of PCBs from the point source is relatively slow due to their low water solubilities, site remediation can be costly due to the expenses incurred by excavation and transportation of the contaminated soil to a hazardous waste site or treatment facility. This has led to interest in developing on-site or in situ soil remediation methods such as high temperature incineration (rotary kiln destruction), soil vitrification, base-catalyzed decomposition (dechlorination) and biodegradation.

One remediation strategy is to mineralize the PCBs to carbon dioxide and chloride ion. Various advanced oxidation processes (AOPs) are being developed which use rapid chemical oxidation techniques for accelerating the destruction of a wide variety of organic pollutants (Bolton et al., 1996; Sedlak and Andren, 1991a, 1991b, 1994; Vollmuth and Niessner, 1995). Lawrence Livermore National Laboratory has developed the remediation technology of hydrous pyrolysis/oxidation (HPO), a novel thermal means of treating polluted soils and groundwater. HPO remediation involves the injection of steam, forming a heated saturated zone which accelerates the destruction of organic contaminants. The basic principle of HPO is the ability of oxygenated hot water to completely oxidize organic contaminants by using the dissolved oxygen in the groundwater as the oxidant (Knauss et al., 1997).

Although HPO was originally targeted towards the remediation of sites contaminated with volatile chlorinated hydrocarbons such as trichloroethane, trichloroethylene, tetrachloroethylene and carbon tetrachloride, additional laboratory experiments have demonstrated that HPO is effective in destroying a wide variety of organic compounds. Chemicals which are representative of several different classes of persistent organic pollutants that have been mineralized in preliminary tests include the following : ethylbenzene (gasoline hydrocarbon), methyl tert-butyl ether or MTBE (fuel oxygenate), naphthalene (creosote component) and pentachlorophenol (fungicide, wood preservative). TCE oxidation is discussed in Knauss, et al. (1997); naphthalene and pentachlorophenol oxidation are discussed in Leif et al. (1997).

The HPO research has been extended to include another class of compounds, the polychlorinated biphenyls, by selecting a representative PCB congener (2,2',3-trichlorobiphenyl) and measuring destruction rates, identifying and quantifying reaction products and determining mass balances at different reaction temperatures. The results of these initial laboratory-based HPO feasibility experiments are presented in this report. A brief discussion of these results is also presented which includes a comparison of the HPO reaction rates for this compound to HPO reaction rates for other pollutants.

Methods

Experimental Methods

Two experiments were performed to study the hydrous pyrolysis / oxidation (HPO) of 2,2',3-trichlorobiphenyl (CAS # 38444-78-9) in phosphate-buffered (pH=7) aqueous solutions. The aqueous buffer solutions were made using distilled, deionized water with the addition of KH_2PO_4 and K_2HPO_4 to result in a neutrally-buffered solution with an ionic strength of 0.033M and $[PO4^{3-}] = 0.0155$ m. Samples of the neat material 2,2',3-Trichlorobiphenyl (>99% pure) were obtained from Ultra Scientific. The experiments were run in Dickson-type, gold-bag rocking autoclaves. These reactors consist of completely water-filled flexible gold bag reactors (approximately 235 mL capacity) with titanium head seals and held at constant pressure by placing the gold reaction cell in large, water-filled super-alloy steel pressure vessels. During the experiment the solution contacts only gold and passivated titanium so unwanted surface catalytic effects are eliminated. Further details on the Dickson system used in these experiments can be found in Knauss, et al. (1997). Descriptions of the two experiments are listed below.

Experiment PCB01 - High PCB Loading

The initial loading of 2,2',3-trichlorobiphenyl in the reactor was 5 mg in 232 mL of water, with 0.270g O_2 added to ensure there was an excess of oxidant. This initial concentration, calculated at 21.6 mg/L, greatly exceeded the aqueous solubility of this PCB congener reported at 0.20 mg/L (Mackay et al., 1992), but complete reactant dissolution was achieved at the elevated reaction temperatures. The vessel was heated according to the following temperature program : 9 days at 131°C, 10 days at 151°C and 18 days at 165°C. An overpressure of 500 psi is maintained throughout the experiment to keep all gases in solution. The progress of the reaction was followed by measuring the aqueous concentrations of 2,2',3-trichlorobiphenyl, total inorganic carbon (reported as dissolved CO_2) and chloride ion.

Experiment PCB02 - Low PCB Loading

The low level PCB stock solution for experiment PCB02 was made by adding an excess of neat 2,2',3-trichlorobiphenyl to the phosphate buffer solution and allowing some of the PCB to dissolve, then filtering this solution to remove any undissolved free product prior to loading. This stock solution had a dissolved oxygen concentration of approximately 8 ppm measured at 25°C, at equilibrium with the atmosphere, providing a stoichiometric excess of oxidant. The vessel was heated to 135°C and monitored for 2,2',3-trichlorobiphenyl concentration.

Analytical Methods

The reactor design allows periodic sampling of the reaction fluids throughout the course of an experiment without disturbing the temperature or pressure of the run. Experimental pressure is held constant by adding or removing distilled water from around the sealed gold bag using a precise constant pressure HPLC syringe pump set at a total pressure of 500 psi, sufficient to keep the system as a single phase. Therefore no headspace exists and all gases remain dissolved in the liquid phase. This makes sampling, and subsequent mass balance calculations, significantly easier.

All samples of the vessel fluids were taken directly in gas-tight syringes equipped with gas-tight valves through a titanium sampling tube with flow controlled by a high-pressure titanium needle valve. Samples taken for total inorganic carbon and dissolved oxygen were analyzed immediately to minimize any loss of volatile components. Samples for gas chromatography were taken in gas-tight syringes containing a known amount of isopropyl alcohol. Sample weight was determined and reported analytical results were corrected for dilution factor. The sampled fluids and dissolved gases were analyzed using a variety of analytical techniques described below.

Analyses of the aqueous organic compounds in PCB01 were conducted on a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector. Samples were introduced by direct injection mode on a 30 m (0.53 mm i.d.) fused silica capillary column coated with methylpolysiloxane (DB-5, J & W Scientific; film thickness 0.5 µm). The GC oven temperature was programmed at isothermal for 2 min. at 60°C, ramped at 12°C/min. to 270°C, and isothermal for 2 min., with helium as the carrier gas. Data were acquired and integrated using Hewlett Packard Chemstation software. Quantitation was done using a multilevel external standard calibration curve. Detection limit for the GC-FID was 0.10 ng/µL.

Analyses of the aqueous organic compounds in PCB02 were conducted on a Hewlett-Packard 5890 gas chromatograph equipped with an electron capture detector. Samples were introduced by direct injection mode on a 30 m (0.53 mm i.d.) fused silica capillary column coated with methylpolysiloxane (DB-5, J & W Scientific; film thickness 0.5 µm). The GC oven temperature was programmed at isothermal for 2 min. at 100°C, ramped at 8°C/min. to 220°C, with helium as the carrier gas and nitrogen make-up flow at 60 mL/min. Data were acquired and integrated using Hewlett Packard Chemstation software. Internal standard method, using a relative response factor, was used to quantitate the PCB concentrations. Detection limit for the GC-ECD was 10 pg/µL.

Gas chromatography-mass spectrometry (GC-MS) was performed on a Hewlett Packard 6890 gas chromatograph equipped with a 30 m x 0.25 mm i.d. HP-5ms (5% phenyl methylsiloxane) capillary column (0.25 µm film thickness) coupled to a Hewlett Packard 6890

Series Mass Selective Detector (MSD) operated in electron impact mode (70eV) over the mass range 35-450 dalton with a cycle time of 1.1 s. The GC oven temperature was programmed at isothermal for 2 min. at 50°C, ramped at 8°C/min. to 300°C, and isothermal for 6.75 min., with the injector at 250°C, and helium as the carrier gas. The MS data were processed using Hewlett Packard Chemstation software. Internal standard method, using a relative response factor, was used to quantitate the PCB concentrations.

Chloride was determined using a Hewlett Packard 1090M HPLC coupled to a Waters 431 conductivity detector. Data were processed using an on-line Hewlett Packard personal computer using Chemstation software. Detection limit for the chloride analyses was 0.02 μg/g.

Total inorganic carbon analyses were obtained using an OI Model 524 analyzer. A weighed sample was injected into a purge vessel containing a 25% phosphoric acid solution which was continuously purged with nitrogen gas. The dissolved inorganic carbon is converted to CO_2 and swept into a non-dispersive infrared detector where the total inorganic carbon, in the form of carbon dioxide, was measured.

Dissolved oxygen in PCB01 was measured by mass spectrometry. Dissolved oxygen in PCB02 was measured using a Microelectrodes Inc. model OM-4 oxygen membrane sensor. The samples were allowed to come to room temperature in a gas-tight syringe before measuring dissolved oxygen to avoid drift due to temperature differences.

Results and Discussion

Experiment PCB01

A partial list of the analytical results for experiment PCB01 is summarized in Table 1. The second column in Table 1 is the elapsed time calculated by defining the time at which the vessel heater is turned on as time 0. Sample PCB01-0 was sampled prior to heating and therefore has a calculated time of -0.10. Fig. 1 is a plot of the aqueous concentrations of 2,2',3-trichlorobiphenyl (PCB), total inorganic carbon (measured as dissolved CO_2) and chloride ion, in μg/g as a function of time (days) for experiment PCB01. Fig. 2 is the same data set plotted using concentration units of mole/kg. From day 0 to day 3 there was a steady increase in the aqueous concentration of PCB, leveling off at approximately 24 μg/g. This aqueous concentration reflects complete dissolution of the 5 mg of PCB initially loaded into the vessel, indicating there was over a 100 fold increase in the aqueous solubility of 2,2',3-trichlorobiphenyl in going from 25°C, where the aqueous solubility is reported at 0.20 μg/g (Mackay et al. 1992), to 130°C.

From day 3 to day 7 there was little change in the PCB concentration but a slight rise in the level of dissolved CO_2 was observed during this time period. Day 7 had the first reported chloride ion level of 0.35 µg/g. A large increase in aqueous concentration of the PCB occurred after day 7 and remained high through day 21. The sudden increase in PCB concentration occurred between day 7 and day 9, while the vessel was still at 131°C, and therefore does not reflect an increase due to an increase in vessel temperature. A definitive explanation for the rise in PCB concentration cannot be given, although we have observed erroneously high aqueous concentrations of sparingly soluble organic compounds under similar conditions, which we have been determined to be due to entrainment of free product present in the sampling valve and transfer tube during sample collection. Under certain circumstances free product may accumulate as the aqueous fluid cools in transit through the sampling tube and valve during sampling.

From the data set no estimate for PCB destruction rate at 131°C can be made due to the slow rate of reaction. After sampling at day 9 the temperature was increased to 151°C. Although no significant drop in PCB concentration occurred, there were noticeable increases in both CO_2 and Cl^- concentrations. After sampling at day 19 the temperature was again increased to 165°C and sampled on four separate occasions before terminating the reaction on day 37.

A substantial amount of PCB destruction occurred at the 165°C temperature, with stoichiometric increases in both CO_2 and Cl^- concentrations. This is shown graphically in Fig. 3, where the concentrations of PCB, CO_2 and Cl^- are plotted as a function of time for the 165°C portion of the experiment. Also plotted are the calculated CO_2 and Cl^- concentrations derived from the changes in the PCB concentration, assuming the reaction goes to completion according to Equation 1:

$$C_{12}H_7Cl_3 + 13O_2 = 12\,CO_2 + 3Cl^- + 3H^+ + 2H_2O. \qquad (1)$$

Fig. 3 shows stoichiometric increases in both CO_2 and Cl^- from the oxidation of the PCB congener 2,2',3-trichlorobiphenyl (within analytical uncertainties) and suggests that the PCB is completely mineralized by HPO under these conditions without a substantial build-up of partially-oxidized intermediates.

Experiment PCB02

The results for this experiment are listed in Table 1. Due to the low initial PCB level in this experiment, neither chloride nor dissolved CO_2 concentrations were measured and only the concentrations of PCB were measured. Fig. 4 is a plot of the data from Table 1. The PCB was destroyed after approximately 2 days at 135°C under these conditions.

Estimated Activation Energy / Comparison of HPO Rates

Fig. 5 is a comparison of HPO reaction rates for the PCB at 151°C and 165°C from experiment PCB01. Due to the uncertainty in measured PCB values in the 151°C range, the losses in PCB shown in Fig. 5 were derived from the corresponding rises in CO_2, with the assumption of complete and instantaneous CO_2 production during PCB destruction. An estimate of E_{act} can be made from the calculated PCB destruction data at 151°C and 165°C. This is shown in Fig. 6. Using the data derived in the Arrhenius plot, a comparison of HPO rates can be made for naphthalene, pentachlorophenol (Leif et al., 1997) and 2,2',3-trichlorobiphenyl; this comparison is summarized in Table 2. Although the rate of pentachlorophenol conversion to tetrachlorophenol is much faster than either the naphthalene or 2,2',3-trichlorobiphenyl destruction, the rate of complete mineralization of pentachlorophenol to CO_2 and Cl^- is substantially slower. Formation of reaction intermediates, or a stepwise reaction such as seen in pentachlorophenol, was not observed during the HPO of naphthalene or 2,2',3-trichlorobiphenyl.

Summary

The novel remediation process of HPO is showing promise as a method for destroying a wide range of organic pollutants in situ. The goal of this research was to broaden the knowledge of HPO chemistry by extending the research to another class of pollutants, the PCBs. Relatively little is known about the physical properties of organic pollutants in aqueous systems at elevated temperatures (Shui et al., 1997), and no information exists regarding the aqueous oxidation of PCBs by HPO. The present work was intended to contribute to the understanding of HPO chemistry.

For a practical application of HPO in a PCB contaminated site, more research is needed to refine reaction rate information and solution effects, such as the roles that other organic species and inorganic components have on the HPO chemistry.

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Table 1. Results from experiments PCB01 and PCB02.

Sample ID	Time [1] (days)	Temperature (°C)	[PCB] [2] (μg/g)	$[CO_2]$ [3] (μg/g)	$[Cl^-]$ (μg/g)
PCB01-0	-0.10	24	0.1	1.58	n.d.
PCB01-1	0.87	130	8.1	2.07	n.d.
PCB01-2	1.78	130	21.8	3.09	n.d.
PCB01-3	2.77	130	24.1	2.94	n.d.
PCB01-5	4.79	131	24.0	3.77	n.d.
PCB01-7	6.79	131	22.6	3.49	0.35
PCB01-9	8.78	131	29.0	3.40	0.51
PCB01-13	12.78	151	28.5	5.16	0.62
PCB01-19	18.80	151	28.4	7.42	1.37
PCB01-21	20.81	165	29.3	10.39	1.45
PCB01-26	25.78	165	22.7	16.76	2.43
PCB01-30	29.80	165	19.8	22.29	3.44
PCB01-37	36.91	165	14.6	31.41	4.88
PCB02-0	-0.92	22	0.460	n.a.	n.a.
PCB02-1	1.00	133	0.497	n.a.	n.a.
PCB02-2	2.00	135	0.232	n.a.	n.a.
PCB02-3	3.00	135	0.014	n.a.	n.a.
PCB02-6	6.01	135	0.024	n.a.	n.a.
PCB02-7	7.02	135	n.d.	n.a.	n.a.
PCB02-8	8.01	135	n.d.	n.a.	n.a.
PCB02-9	9.05	135	n.d.	n.a.	n.a.

n.d. : not detected

n.a. : not analyzed

1 : determined relative to start of initial heating

2 : [PCB] = [2,2',3-trichlorobiphenyl]

3 : $[CO_2]$ = concentration of total inorganic carbon, reported as ug CO_2 / g solution

Table 2. HPO rates for naphthalene, pentachlorophenol and 2,2',3-trichlorobiphenyl.

Naphthalene

T (°C)	T (K)	1/T (K)	log rate (mol/kg-s)	rate (mol/kg-s)	rate (ug/kg-d)
100	373	2.68E-03	-11.35	4.51E-12	50.0
125	398	2.51E-03	-10.50	3.14E-11	348.0
150	423	2.36E-03	-9.76	1.74E-10	1926.6

Pentachlorophenol (rate calculated from loss of pentachlorophenol, major product is tetrachlorophenol)

T (°C)	T (K)	1/T (K)	log rate (mol/kg-s)	rate (mol/kg-s)	rate (ug/kg-d)
100	373	2.68E-03	-10.23	5.88E-11	1353.8
125	398	2.51E-03	-9.48	3.27E-10	7533.4
150	423	2.36E-03	-8.83	1.49E-09	34222.5

PCP (complete mineralization to carbon dioxide, rate calculated from carbon dioxide production)

T (°C)	T (K)	1/T (K)	log rate (mol/kg-s)	rate (mol/kg-s)	rate (ug/kg-d)
100	373	2.68E-03	-11.18	6.54E-12	150.4
125	398	2.51E-03	-10.21	6.10E-11	1404.1
150	423	2.36E-03	-9.36	4.37E-10	10063.7

2,2'-3-Trichlorobiphenyl

T (°C)	T (K)	1/T (K)	log rate (mol/kg-s)	rate (mol/kg-s)	rate (ug/kg-d)
100	373	2.68E-03	-13.15	7.14E-14	1.6
125	398	2.51E-03	-12.05	8.88E-13	19.8
150	423	2.36E-03	-11.09	8.20E-12	182.4

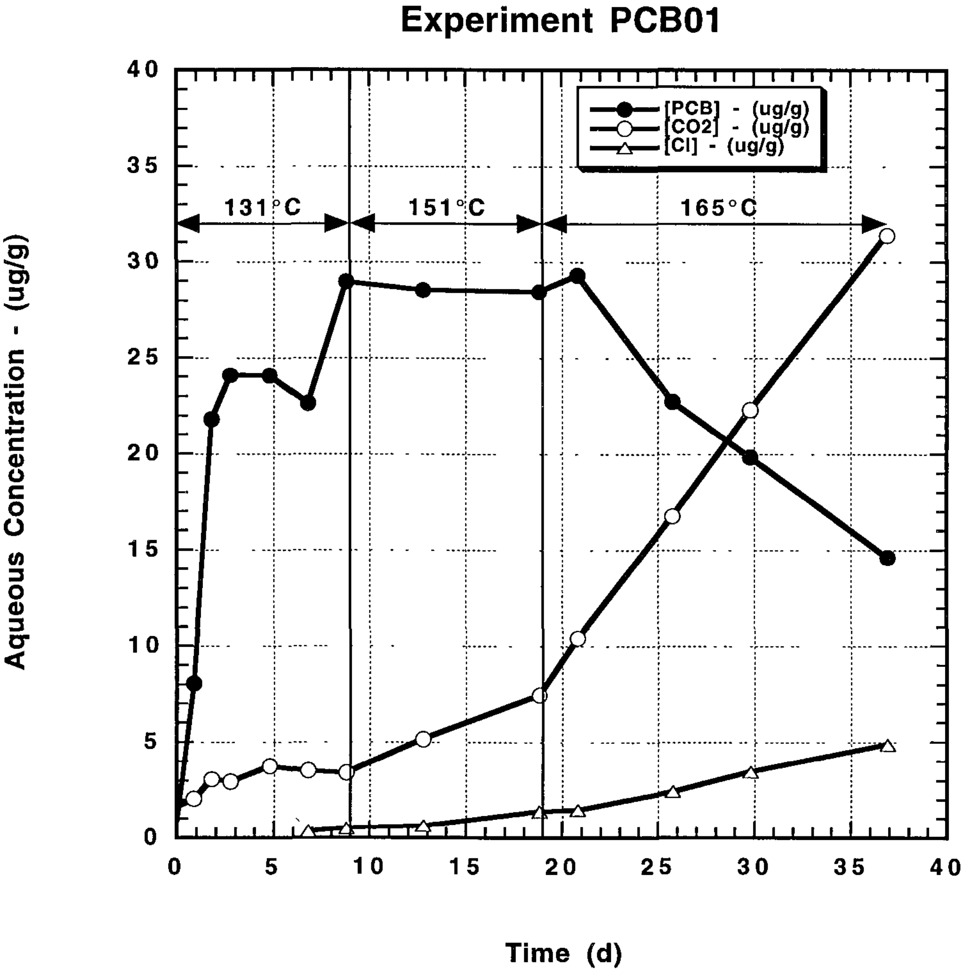

Figure 1. PCB (2,2',3-trichlorobiphenyl) destruction, total inorganic carbon production (reported as CO_2) and chloride ion production vs. time during experiment PCB01, reported in concentration units of µg/g.

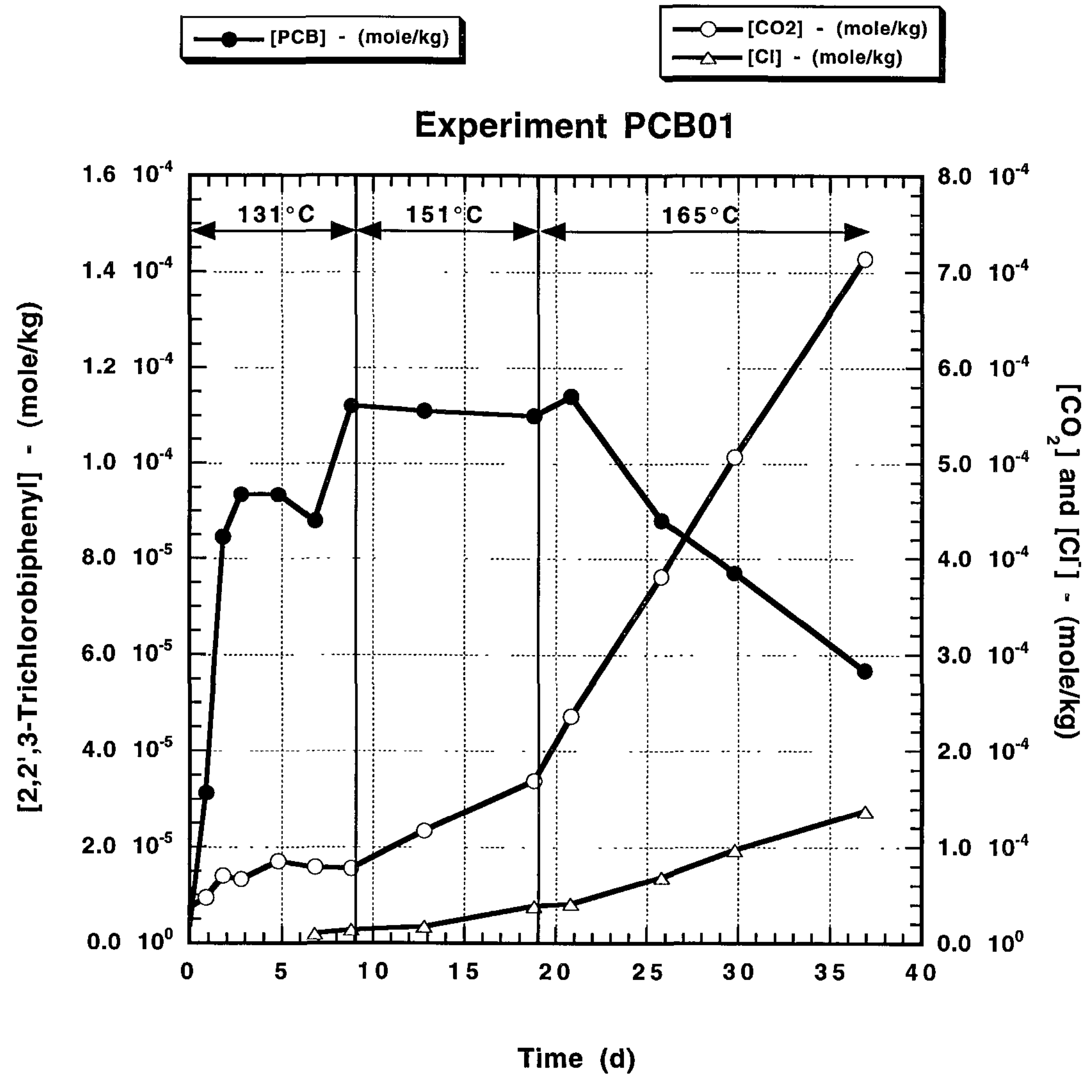

Figure 2. PCB (2,2',3-trichlorobiphenyl) destruction, total inorganic carbon production (reported as CO_2) and chloride ion production vs. time during experiment PCB01, reported in concentration units of mole/kg.

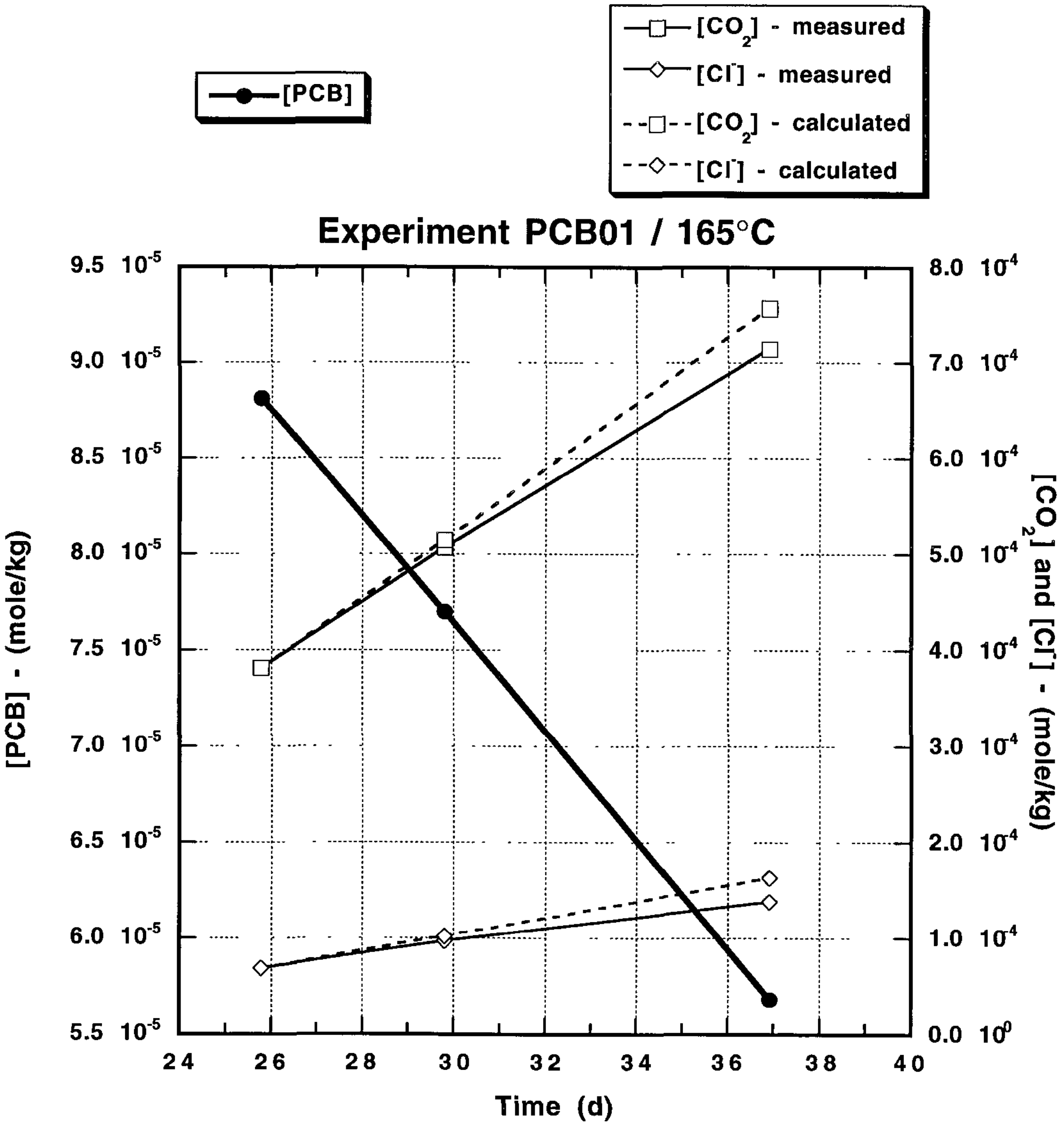

Figure 3. Measured and calculated concentrations for production of total inorganic carbon (reported as CO_2) and chloride ion during HPO of 2,2',3-trichlorobiphenyl at 165°C.

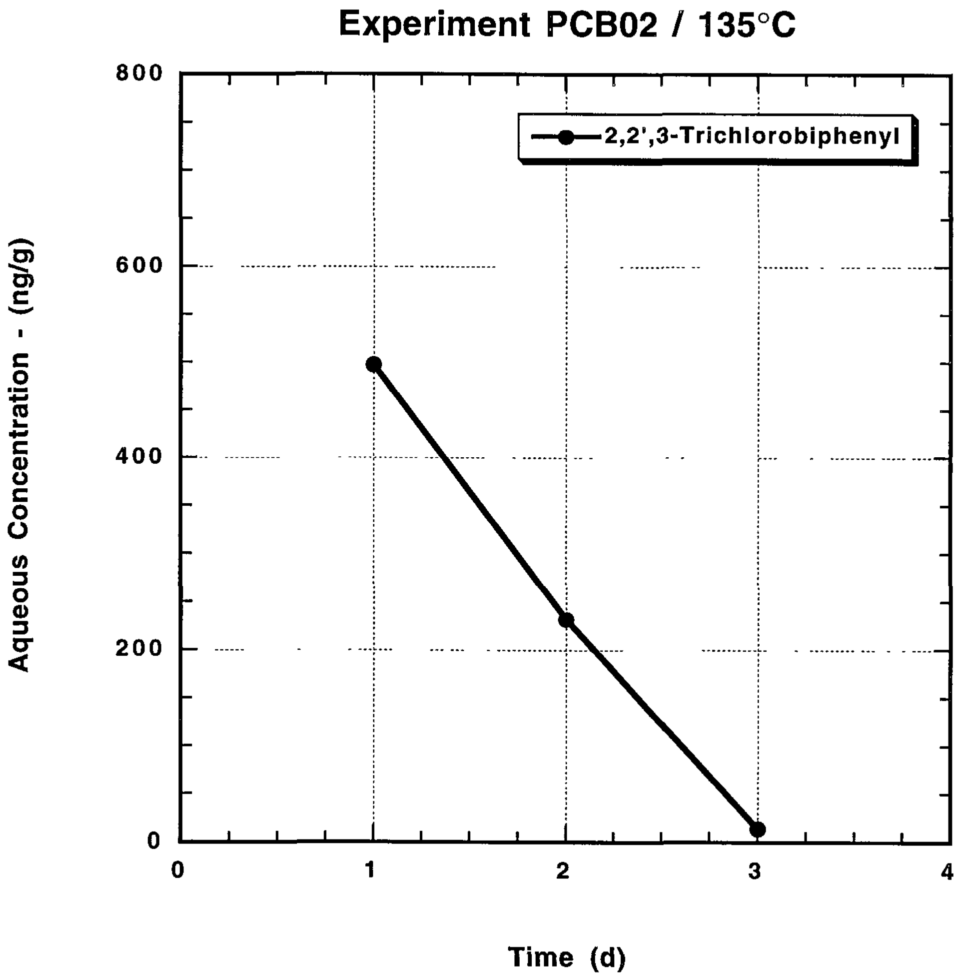

Figure 4. PCB (2,2',3-trichlorobiphenyl) vs. time during experiment PCB02, reported in concentration units of ng/g.

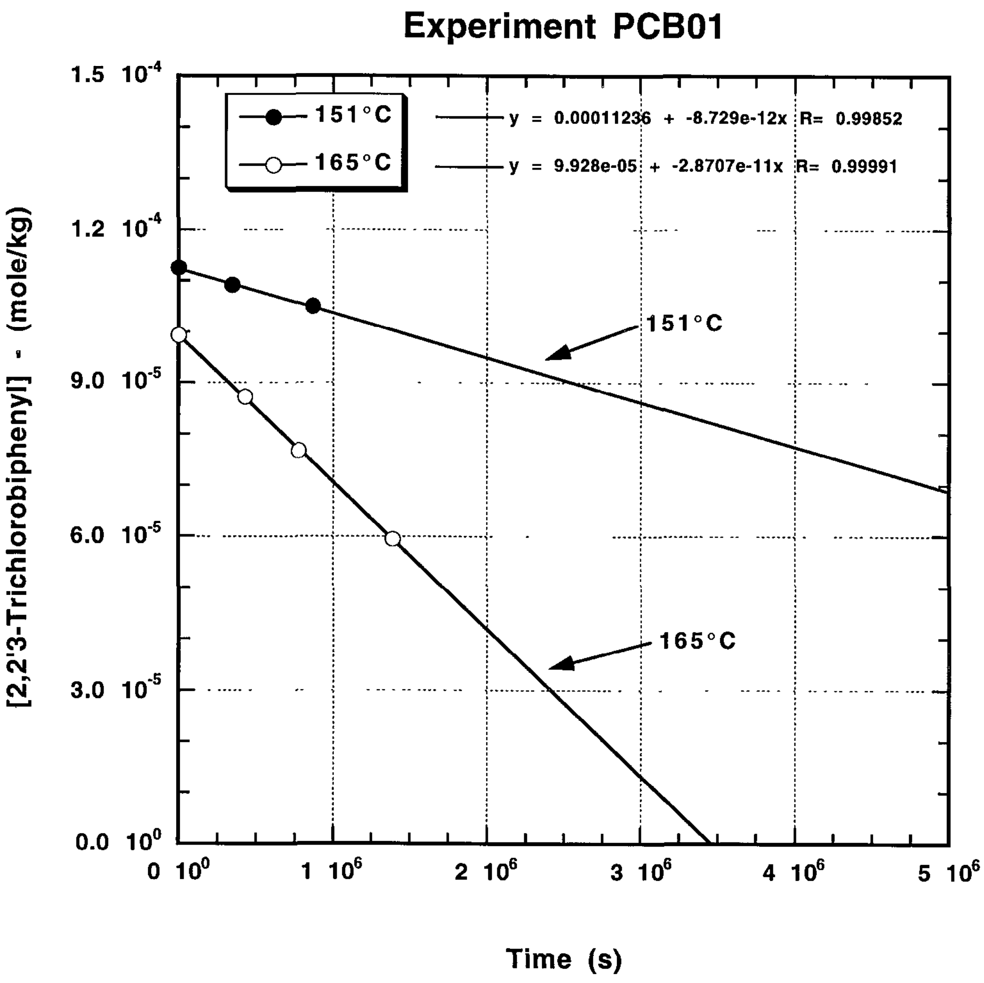

Figure 5. Calculated changes in 2,2’,3-trichlorobiphenyl as a function of time based on the production of total inorganic carbon (reported as CO_2).

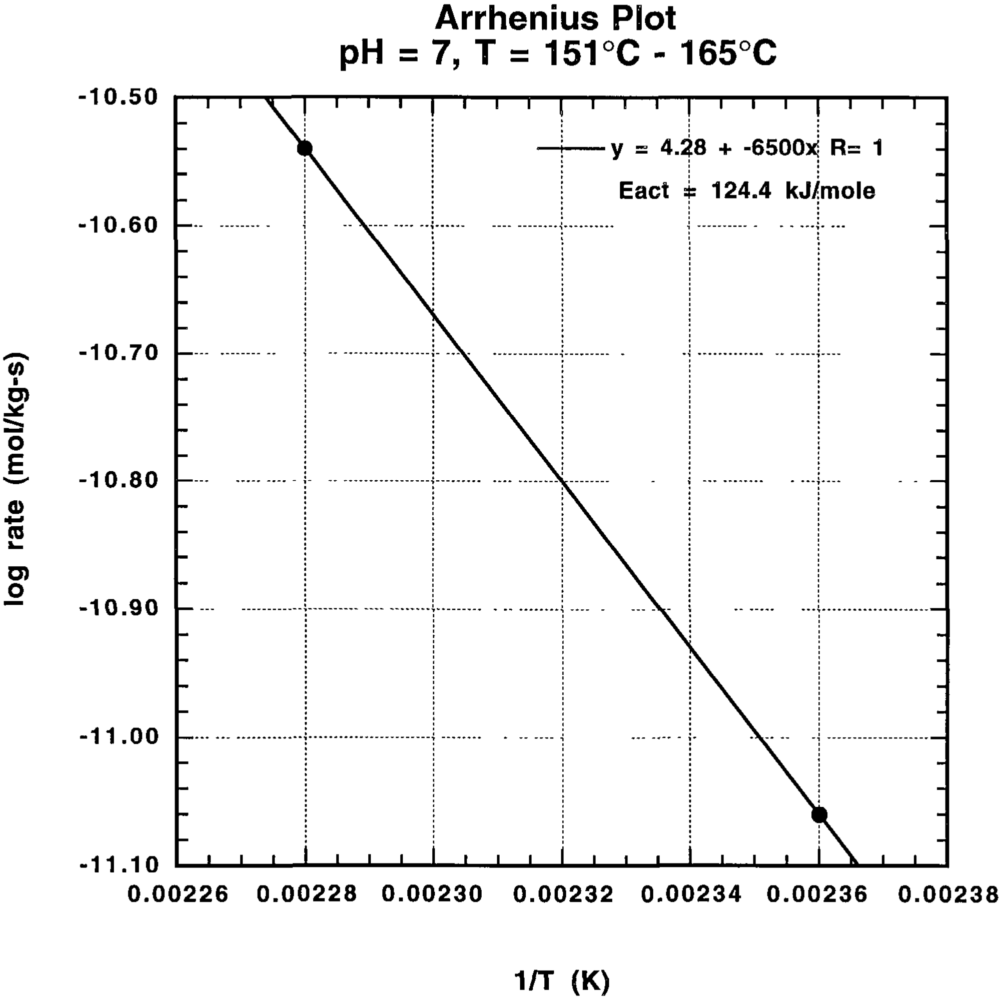

Figure 6. Arrhenius plot for 2,2',3-trichlorobiphenyl from data generated in experiment PCB01.

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