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Formation of octachloroacenaphthylene in the pyrolysis of decachlorobiphenyl

A. Bleise, E. Kleist, K. Günther[1], and M.J. Schwuger

Institut für Angewandte Physikalische Chemie
Forschungszentrum Jülich GmbH, Germany

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Abstract

The pyrolytic degradation of decachlorobiphenyl (PCB 209) in the temperature range of 700 - 1000°C and at a pyrolysis time of 10 seconds generated one main chloroaromatic product. This compound has been identified by HPLC-UV, GC-MS, GC-FTIR and ^{13}C-NMR as octachloroacenaphthylene (OCAN).
The mechanism of the nearly quantitative formation of octachloroacenaphthylene (OCAN) occurs via a nonachlorobenzobarrylene radical (Z1R) as an intermediate followed by a rearrangement and further dechlorination to form OCAN. Calculations with the program THERM based on the Benson-group-theory indicated that this mechanism is not possible for lower or nonchlorinated biphenyls. © 1997 Elsevier Science Ltd

Introduction

Perchlorinated aromatic compounds are thermally most stable organic substances [1.]. The thermal destruction of perchlorinated compounds requires extreme conditions. In addition most of them are inert to chemical and biological degradation [2.] and are accumulated in the environment as well as in adipose tissue.

Perchlorinated aromatic substances are thermally formed from aliphatic and olefinic precursors [3. - 5.], or by chlorination of lower chlorinated congeners [6.; 7.]. An increasing amount of these compounds is observed in combustion processes with rising temperature due to their favoured thermodynamic formation [7.; 8.]. The thermal behaviour of these substances is therefore of special interest. Perchlorinated substances are appropriate compounds for testing the efficiency of the degradation of organic substances in thermal processes [9.; 10.].

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[1] to whom correspondence should be adressed

Perchlorinated acenaphthylene was formed in our pyrolysis experiments with different chlorinated compounds (e.g. tetrachlorobenzene, pentachlorobenzene, hexachlorobenzene, hexachlorobutadiene, tetrachloroethylene) [11.]. The pyrolytical degradation of PCB 209 showed extremely high concentrations of OCAN .

This paper describes the pyrolysis of PCB 209 at 700 °C - 1000 °C with residence times of 10 seconds and 10 minutes. OCAN, the main chlororganic product, is identified and characterized. The mechanism of formation of octachloroacenaphthylene is discussed and thermodynamically calculated.

Experimental section

All chemicals were obtained from commercial sources. They were used without further purification.

The pyrolytic experiments were performed in an infrared heated tube furnace F420 IO RPD of STROEHLEIN INSTRUMENTS with a quartz tube of 15 mm inner diameter and 19 cm length. The temperature was regulated by a PID-Controller 100 and measured with NiCr-Ni thermocouples. Fig. 1 shows the system for the pyrolysis experiments.

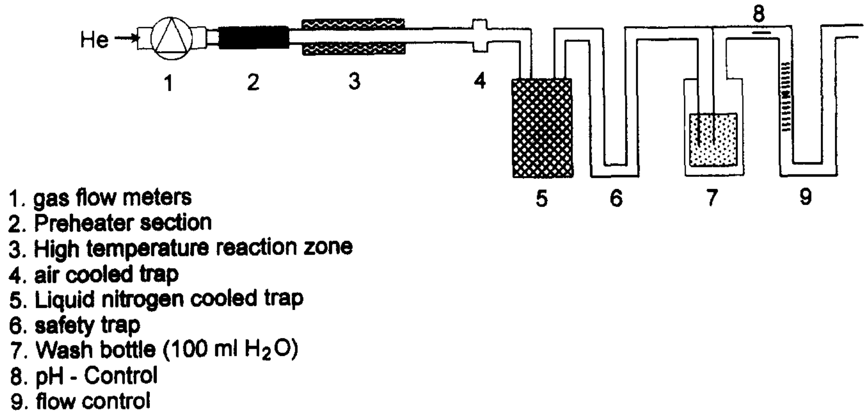

Fig. 1

PCB 209 was synthesized by $FeCl_3$ catalysed chlorination of biphenyl. The chlororganic compound (50-200mg) were introduced on a crucible in the preheating zone (2) and heated up to 350 °C. The evaporated substances are carried by helium 6.0 to the pyrolysis region (3). The pyrolysis products were trapped by different cold traps and wash bottles (5-7).

The high boiling chloroaromatic products were found in the first, air cooled trap (4) and directly measured by GC-FID after dissolving in toluene (Nanograde; Promochem, Wesel). Further studies in sealed quartz ampoules were performed. 10-20 mg of the chlororganic compounds were heated in the ampoules at the pyrolysis temperature (10 minutes). After fast cooling by liquid nitrogen, the ampoules were opened and extracted with toluene in an ultrasonic bath (10 minutes).

Identification, characterization and quantification of the products were performed by different chromatographic techniques.The samples were subjected to the following analyses : gas chromatography (GC) with flame ionisation detection (FID), with mass spectroscopy and high performance liquid chromatography (HPLC) with ultraviolet-visible (UV-VIS) absorption detection. All of the GC work was performed on HEWLETT-PACKARD model 5890 series 2 systems with split injector (splitless 1 min.; split 1:10) and electronic flow control (EPS). The fused silica capillary columns were 60 m long with 0.32 mm inner diameter and a 0.25 μm thick film (DB-5, J & W Scientific). The GC oven temperature was programmed to run after 3 minutes hold at 60 °C from 60 °C to 180° C at 8°/min. 2 minutes hold; from 180 °C to 210° C at 2°/min. 2 minutes hold; from 210 °C to 300° C at 10°/min. 15 minutes hold. Helium was used as carrier gas. The mass spectrometer was an Unicam Automass 150.

For the HPLC-analysis the samples are concentrated by a gentle nitrogen stream and dissolved in acetonitrile. Identification is made by UV-detection and comparision of the spectra with the nonchlorinated substances. The HPLC-system consists of a gradient pump (Spectra Physics SP8800), a LichroCART RP 18 column (Merck, Darmstadt, length 250 mm, ID 4 mm) and a diode array detector (Perkin Elmer, range 190-430 nm, resolution 1 nm). The injected volume was 10μl and the flow rate of the isocratic run (acetronitril/water 90 : 10) 1 ml/min. at 20 °C.

The ^{13}C-NMR spectrum was observed on a BRUKER AMX 400 WB spectrometer under the following conditions : frequency 100 MHz, pulse repetition 6 s, 9000 scans. $CDCl_3$ with a small amount of TMS was used as solvent. The concentration of the sample was only 3 mmol.

The GC-FID chromatogram showed the product distribution and concentrations. GC/MS proved to be valuable in determinig the molecular formula. The number of chlorine atoms is distinguished by its isotope abundance distribution. But the GC-MS spectrum did not provide sufficient information to differentiate isomers. The HPLC UV-detection is needed to identify the chlororganic substance classes. The ^{13}C-NMR spectrum and the FTIR spectrum characterize the compound, proving unequivocally the structure.

Results and discussion

Pyrolysis experiments with several highly chlorinated compounds confirmed the formation of octachloroacenaphthylene (OCAN), but always in combinition with decachlorobiphenyl (PCB 209). For this reason our investigations were expanded using PCB 209 as an educt. This pyrolysis produced only OCAN and hexachlorobenzene (HCB) as chlororganic substances in higher concentrations. Fig. 2A shows the effect of temperature on the pyrolytic destruction of PCB 209 and the product distribution.

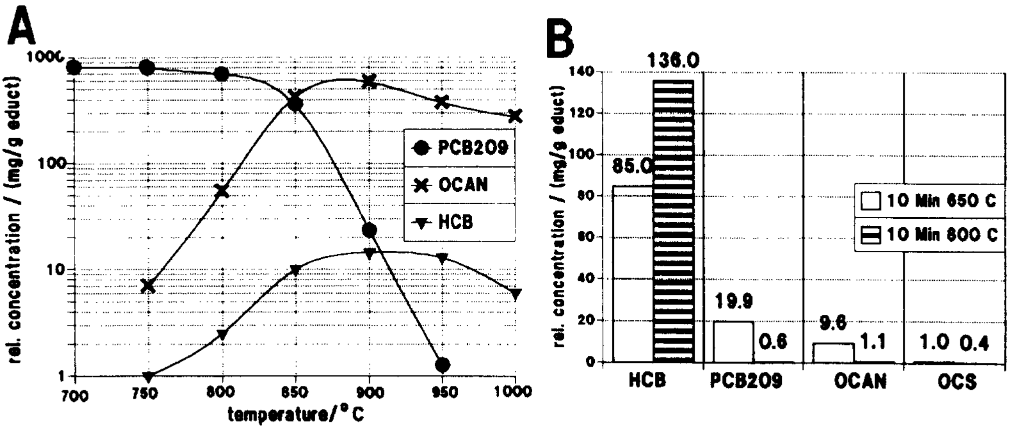

Fig. 2. **PCB 209-Pyrolysis:**
A : Pyrolysis products with a residence time of 10 seconds
B : Pyrolysis products in sealed ampoules with a pyrolysis time of 10 minutes

With a residence time of 10 seconds the pyrolytic degradation of PCB 209 starts at temperatures of about 800 °C. At 1000 °C the destruction is quantitative. Octachloronaphthalene (OCN) is not detected because of the high temperatures needed for the PCB 209 destruction. The sum of formed OCAN and the educt appears to be constant up to temperatures of 950 °C. At temperatures of about 900 °C the thermal conversion of

PCB 209 to OCAN is approximately 80 %. It was possible to isolate the octachloroacenaphthylene at this conditions for further characterizations. The OCAN is produced in long red needles and condenses in the first, air-cooled trap.

An increase of the pyrolysis time in sealed quartz ampoules leads to a different product distributions. Temperatures of 700 °C and pyrolysis times of 10 minutes already result in a complete degradation of the educt and formation of OCAN and HCB. Under these conditions HCB is the main product (Fig. 2B). Some C_2-fragments as perchloroethane, tetrachloroethylene and octachlorostyrene (OCS) are formed also.

Characterization and identification of octachloroacenaphthylene (OCAN)

Octachloroacenaphthylene (OCAN) is the most abundant compound found in pyrolysis experiments of PCB 209 between temperatures of 750 - 1000 °C. It has a remarkable thermal stability with pyrolysis times of a few seconds. OCAN has been detected before in pyrolysis samples of HCB and tetrachloroethylene [5.; 12.]. The destruction of OCAN starts at temperatures above 900 °C (Fig. 2). The MS fragmentation patterns of chlorinated acenaphthylenes and chlorinated biphenylenes are identical [13.] making a positive identification impossible (mass spectrum of OCAN Fig. 3, FT-IR spectrum of OCAN Fig. 4).

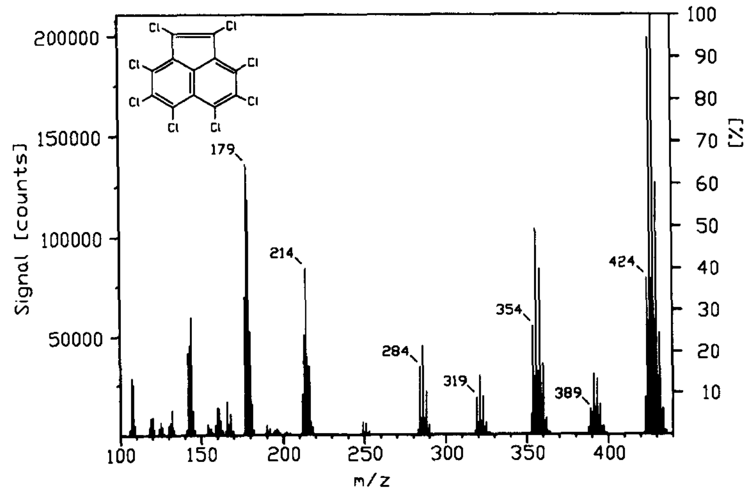

Fig. 3. Mass spectrum of Octachloroacenaphthylene (OCAN)

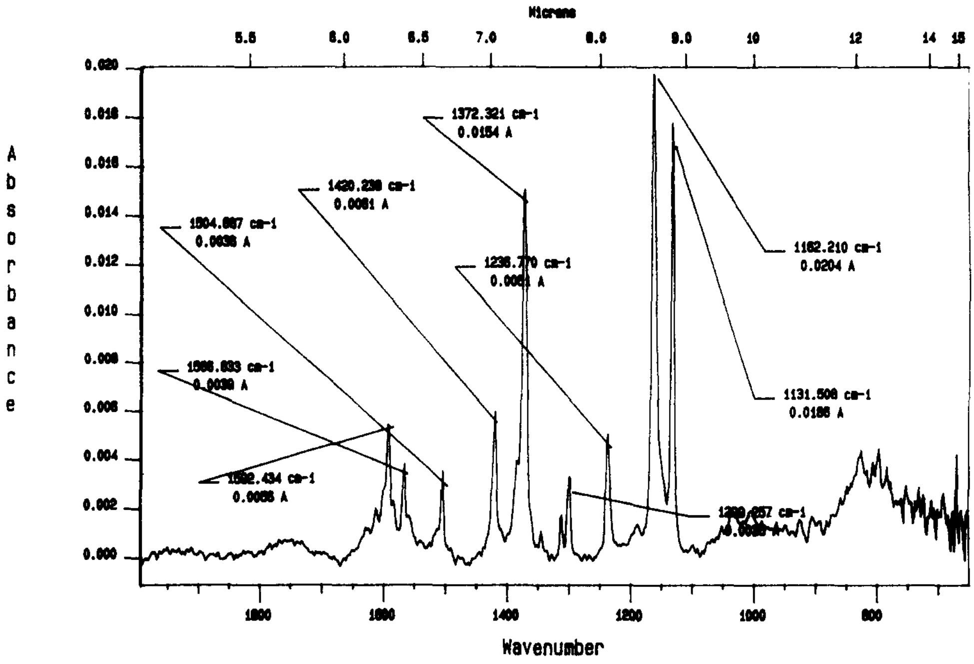

Fig. 4. FT-Infrared spectrum of Octachloroacenaphthylene (OCAN)

Other methodes are needed to classify these compounds. Separation from structural isomeric octachlorobiphenylene and identification of octachloroacenaphthylene is made by comparison of the UV-spectra. The measured UV-spectra of the nonchlorinated acenaphthylene and the perchlorinated substance in the pyrolysis samples are presented in Fig. 5. The UV-bands show a hypochromic shift by chlorination, the extinction coefficient is smaller and the fine structure depressed, but the form of the adsorption bands is the same. Characterization of OCAN is made by ^{13}C-NMR and FTIR. Seven magnetically different carbon atoms are found in acenaphthylenes while there are only three in biphenylenes. Fig. 5 presents the measured ^{13}C-NMR spectrum of OCAN. Perchlorinating of aromatic compounds causes a low field shift of the chlorosubstituted aromtic carbons of approximately 5 ppm [14.; 15.]. The quarternary carbons are deshielded and high field shifted. The ^{13}C-NMR shows unambigiously that octachloroacenaphthylene and not octachlorobiphenylene is formed in the pyrolysis of PCB 209. But all other thermal products with the formula $C_{12}Cl_xH_{8-x}$ in the pyrolysis experiments of chlorinated benzenes proved to be structurally isomeric chlorinated biphenylenes [13.]. 135 possible chlorinated acenaphthylenes exist, but only the perchlorinated octachloroacenaphthylene is thermally formed from highly chlorinated aromatic and olefinic compounds.

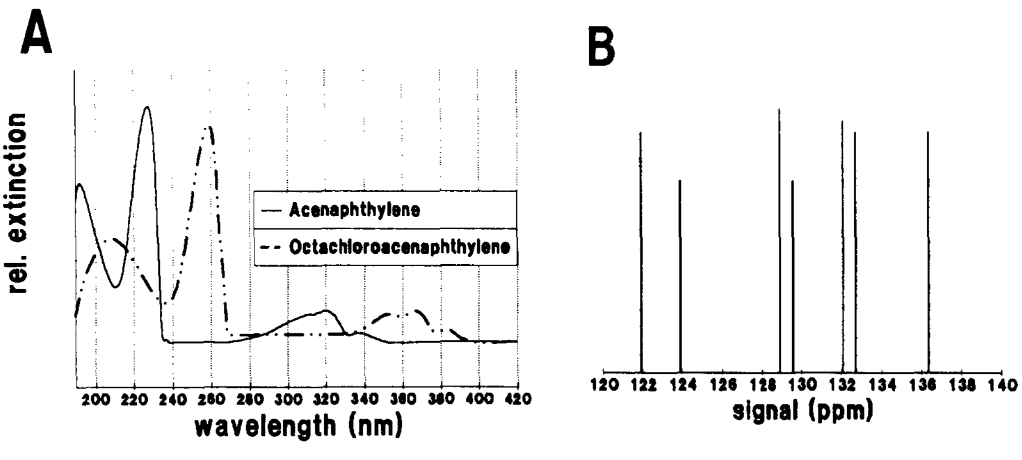

Fig. 5. **Octachloroacenaphthylene (OCAN):**
A : UV-Spectra of acenaphthylene and octachloroacenaphthylene (OCAN)
B : ^{13}C-NMR-spectrum of OCAN

OCAN is a planar molecule (symmetry group C_{2v}) with a naphthalene framework and a strongly conjugated double bond [16.]. These conjugation and the eight chlorine atoms directly attached to the π-system desactivate the double bond towards electrophilic attack.

Mechanism of OCAN formation in the pyrolysis of PCB 209

The formation of octachloroacenaphthylene (OCAN) in pyrolysis experiments has been reported before [5.; 12.; 17.]. J. A. Mulholland et. al. detected OCAN and other perchlorinated aromatics in pyrolysis samples of trichloroethylene. He explained the formation of perchlorinated aromatic compounds by the addition of dichloroacetylene (C_2Cl_2) primarily generated by elimination of HCl. This C_2-addition mechanism (**C_2-mechanism**) producing perchloroaromatic substances of even carbon number is analogous to the formation and growth of hydrocarbon aromatic compounds [18.]. The formation of aromatic compounds in thermal reactions by C_2-mechanisms is a well known thermal reaction [19., 20.]. In this pathway octachlorostyrene (OCS) and

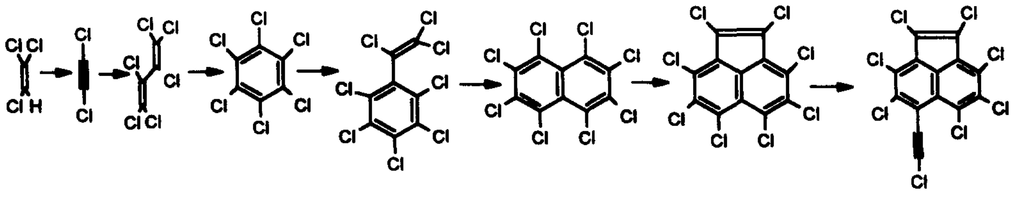

Fig. 6. OCAN-formation: Thermal C_2-mechanism [17.]

octachloronaphthalene (OCN) are intermediates for the formation of octachloroacenaphthylene. OCAN is not a significant end product. It is also an intermediate in the generation of chlorinated aromatic hydrocarbons (Fig. 6). In contrast OCAN is found in the samples in large concentrations while OCN and OCS could not be detected in any pyrolysis samples (Fig. 7).

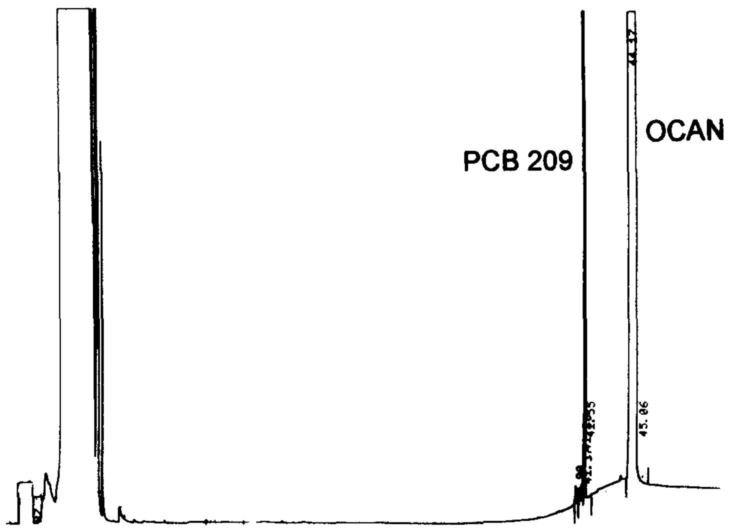

Fig. 7. Chromatogram of a PCB 209 pyrolysis sample:
Pyrolytical conditions: 900 °C, 10 seconds residue time

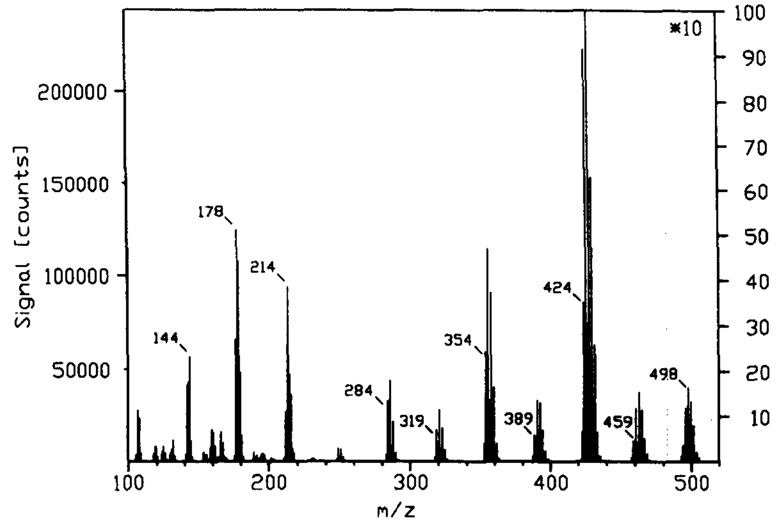

Fig. 8. **Mass spectrum of the intermediate (Z1):** Pyrolytic conditions: 900 °C, 10 seconds residue time

The analysis of concentrated samples showed a product with the same composition as the educt ($C_{12}Cl_{10}$). Due to a fast abstraction of 2 chlorine atoms the molecular peak is difficult to detect in the mass spectrum (Fig. 8). Because of this fast fragmentation a tricyclic structure is postulated for this substance (Decachlorobenzobarrylene *Z1*). As there are no aromatic nor aliphatic molecules found in equal concentrations over the whole investigated temperature range rearrangement from PCB 209 to OCAN is the only possible reaction. The results can be explained starting with radical dechlorination of PCB 209 followed by a conversion of the radical to the nonachlorobenzobarrylene radical ($C_{12}Cl_9^{\cdot}$; **Z1R**). This intermediate is stabilized by another rearrangement and subsequent dechlorination to form OCAN. This pathway is presented in Fig. 9.

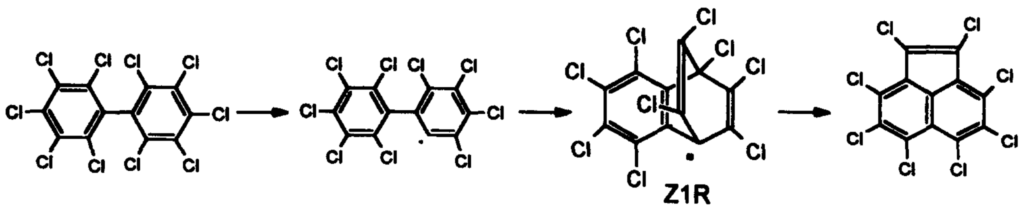

Fig. 9. **PCB 209-pyrolysis:** mechanism of the OCAN formation

In the gaseous and liquid state PCB 209 is a non planar molecule. The four chlorine substituents in ortho position cause a twisted conformation. The observed twisting angle results from two opposite effects, the delocalisation of aromatic π electrons and steric repulsion of the ortho chlorine atoms. This geometry makes a rearrangement of the primarily formed ortho radical (1) to Z1R steric possible. In addition the formed radical of decachlorobenzobarrylene is resonance stabilised.

The steps for the formation of OCAN in the PCB 209 pyrolysis are calculated applying the Benson-group-theory [24.; 25.]. The thermodynamic data are calculated with the program THERM [26.] from the Institute of Technology at the University of New Jersey (New Jersey; NJ; USA). The thermodynamic reaction data in dependence on the temperature are listed in Tab. 1 and are compared with the same reaction of the nonchlorinated substances (R4)

$$\text{PCB 209} \rightarrow C_{12}Cl_9^{\cdot} + Cl^{\cdot} \qquad \textit{(R1)}$$

$$C_{12}H_{10} \rightarrow C_{12}H_9^{\cdot} + H^{\cdot} \qquad \textit{(R2)}$$

	(*R1*) 300 K	(*R2*) 300 K	(*R1*) 1000 K	(*R2*) 1000 K
ΔH_R(kJ/Mol)	372.1	475.5	480.7	496.5
ΔG_R(kJ/Mol)	317.4	434.7	180.9	333.4
ΔS_R(J/mol K)	182.4	136.3	202.8	147.3

Tab. 1. Thermodynamic reaction data of reaction R1 and R2

$$C_{12}Cl_9^{\cdot} \rightarrow \text{Z1R} \qquad \textit{(R3)}$$

$$C_{12}H_9^{\cdot} \rightarrow \text{Z2R} \qquad \textit{(R4)}$$

	(*R3*) 300 K	(*R4*) 300 K	(*R3*) 1000 K	(*R4*) 1000 K
ΔH_R(kJ/Mol)	-63.5	27.9	-79.4	15.8
ΔG_R(kJ/Mol)	-51.9	39.2	-13.8	75.0
ΔS_R (J/mol K)	-38.7	-37.6	-65.6	-59.1

Tab. 2. Thermodynamic reaction data of reaction R3 and R4

An intermediate of structure Z1 (chlorinated benzobarrylene) is discussed in the literature as a precursor of the thermal formation of chlorinated naphthalenes [21.]. These tricyclic compounds react thermally in a Retro-Diels-Alder reaction by eliminating chloroacetylenes to form the chlorinated naphthalenes. The formation of a similar stressed molecule is reported by H.D. Martin [22.]. Thermodynamic calculation based on the Benson-group-theory [23.] showed a concerted Retro-Diels-Alder reaction mechanism for the conversion of barrylene (bicyclo[2.2.2]octa-2,5,7-trien) to acetylene and benzene. A radical pathway with an biradical as intermediate is excluded by this calculation results.

The crucial step in the formation of OCAN from PCB 209 is the radical rearrangement to Z1R. This reaction is for nonchlorinated compounds thermodynamically unfavourable (Tab. 2) caused by lack of stabilization of the radical by the chlorine substituents. In addition there is a steric hindrance of the nearly planar biphenyl radical to attack the para-position of the neighbouring phenyl ring.

Conclusions

The thermal destruction of PCB 209 shows OCAN as the most abundant product. Only two other chlorinated aromatic compounds, hexachlorobenzene and in small amounts decachlorobenzobarrylene are found as by-products. The distingtion of OCAN from structural isomeric chlorinated biphenylenes is achieved by comparison of the UV-spectra of OCAN and the nonchlorinated acenaphthylene. The characterization is made by ^{13}C-NMR and FTIR.

A mechanism via radical rearrangements and step-wise dechlorination instead of the usually postulated C_2-mechanism is formulated for this reaction. Calculations based on the Benson-group-theory showed that this mechanistic pathway is in contrast to the nonchlorinated molecules thermodynamically possible. The chlorine substituents stabilize the radical and the non planar geometry of PCB 209 favours this radical rearrangement. OCAN is the only chlorinated acenaphthylene detected in several pyrolysis samples. It is always found in combination with PCB 209.

Up to now there are no data about the toxicidy available for this compound, which is usually weaker for the perchlorinated substances than for lower chlorinated congeners.

Acknowledgements

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