

FORMATION OF CHLORINATED BENZO[A]PYRENES DURING COMBUSTION OF POLYSTYRENE IN AN AIR/CL₂-MIXTURE

Marinos N, Rotard W D

Institut für Technischen Umweltschutz, Sekr. KF3, Technische Universität Berlin,
Strasse des 17. Juni 135, D-10623 Berlin, Germany

Abstract

Mono-, di-, tri- und tetrachlorinated benzo[a]pyrenes were synthesized as reference compounds and an analytical method developed for the substance class. On burning polystyrene in a chlorous atmosphere, mono-, di- and trichlorinated benzo[a]pyrenes could be quantitatively detected in relevant amounts.

Introduction

Analytical techniques to investigate the spread, distribution, effects, characteristics, sources and conditions of formation as well as the fate of polyaromatic hydrocarbons (PAHs) and their nitro- resp. nitrooxo-derivates have been developed over the last four decades.

Because of their ubiquitous distribution and relatively high daily intake, especially via particular foodstuffs (grill, roast, toast etc.) and tobacco smoke, as well as their mutagenic and in some cases also carcinogenic effects, they are still of significant public interest with efforts being made to reduce human uptake through regulatory means¹⁻¹⁰.

Because chlorine radicals may be produced during the burning of chlorous substances, it seems likely that these could react with PAHs to form chlorinated polyaromatic hydrocarbons (Cl-PAHs). Cl-PAHs could indeed be detected in air-, water- and sediment samples over the last few years¹¹. Cl-PAHs possessing three to seven rings could be detected in fly ash from refuse incinerators for radioactive waste¹² - the concentrations were comparable to those of the PAHs. Cl-PAHs were also detected in car exhaust, snow, country air¹³ and 40 pg/m³ in road tunnels and 10 pg/m³ at roadsides¹⁴. Furthermore, Cl-PAHs were found in flue gases from coal power stations as well as communal refuse incinerators^{15,16}. Cl-PAHs are also generated when PVC is burned¹⁷, and Cl-PAHs were detected in the air¹⁸⁻²⁰. Water chlorination, including that of contaminated seawater also leads to the formation of Cl-PAH²¹⁻²⁴.

Chlorinated pyrenes²⁵ and 7-chlorobenzo[a]anthracene (Cl-BaA)²⁶ are mutagenic, additionally Cl-PAHs possess DNA-altering characteristics²⁷ and some are active Ah-receptors²⁸. Furthermore, microorganisms are not only capable of metabolising chlorinated benzo[a]pyrenes (Cl-BaPs) but also creating Cl-PAHs as well²⁹.

Since little is known to date about the formation and environmental effects of four ringed Cl-PAHs, our aim was to investigate the formation of Cl-BaPs during the incineration of polystyrene.

Materials and Methods

Synthesis of 6-chlorobenzo[a]pyrene

204,8 mg (0,8 mmol) benzo[a]pyrene (BaP) in 20 ml tetrachloromethane (CCl₄) were placed into a two-necked flask and cooled to -10°C. A total of 85,2 mg (1,2 mmol) chlorine gas (Cl₂) dissolved in CCl₄ was then added in 8 mg aliquots stepwise every 20 min with a µL syringe. The precipitate was filtered out, washed three times with a little cold (4°C) CCl₄ and then crystallised out of the CCl₄ for purification. This yielded 25 mg of a yellow-brown powder (12,5 %); MS: m/z 286 [Cl-BaP]⁺, m/z 250 [Cl-BaP-HCl]⁺, m/z 224 [Cl-BaP-HCl-C₂H₂]⁺, m/z 143 [Cl-BaP]⁺⁺, m/z 125 [Cl-BaP-HCl]⁺⁺.

Synthesis of 3,6-dichlorobenzo[a]pyrene

Similarly to the above procedure, a total of 42,6 mg (0,6 mmol) Cl₂ was added to 49,1 mg (0,2 mmol) BaP in 10 ml CCl₄ with stirring. The precipitate was washed alternately twice with each of a little cold CCl₄ and trichloromethane (CHCl₃) and subsequently recrystallised. Yield was 77 mg orange powder (50 %); MS: m/z

320 [Cl₂-BaP]⁺, m/z 284 [Cl₂-BaP-HCl]⁺, m/z 250 [Cl₂-BaP-2Cl]⁺, m/z 160 [Cl₂-BaP]⁺⁺, m/z 125 [Cl₂-BaP-2Cl]⁺⁺.

Synthesis of trichlorobenzo[a]pyrenes

To 25,6 mg (0,1 mmol) BaP in 2 ml CCl₄, 3 aliquots, each 5ml, of a Cl₂-saturated CCl₄-solution were added at 30 min intervals at room temperature with stirring. Stirring was continued overnight. The precipitate was filter off, washed twice alternately with each of a little cold CCl₄ and trichloromethane (CHCl₃). A caramel coloured solid was formed containing trichlorobenzo[a]pyrene isomers, 3,6-Cl₂-BaP and a few tetrachlorobenzo[a] pyrene isomers; MS: m/z 354 [Cl₃-BaP]⁺, m/z 318 [Cl₃-BaP-HCl]⁺, m/z 284 [Cl₃-BaP-2Cl]⁺, m/z 224 [Cl₃-BaP-2Cl-HCl-C₂H₂]⁺, m/z 177 [Cl₂-BaP]⁺⁺, m/z 142 [Cl₃-BaP-Cl]⁺⁺.

Synthesis of tetrachlorobenzo[a]pyrenes

5 ml of a saturated solution of chlorine in CCl₄ in was added to 35 mg (0,14 mmol) BaP in 10 ml CCl₄ at room temperature with stirring. After one hour, the mixture was warmed to 50°C and every ½ h 5ml saturated CCl₄ solution added. After 5 hours the supernatant was poured off and the remainder washed twice with a little cold CHCl₃. A yellow, highly viscous fluid, mainly of tetrachlorobenzo[a]pyrene isomers und a few trichlorobenzo[a] pyrene isomers; MS: m/z 390 [Cl₄-BaP]⁺, m/z 318 [Cl₄-BaP-2HCl]⁺, m/z 282 [Cl₂-BaP-HCl]⁺, m/z 248 [Cl₄-BaP-2 HCl-2Cl]⁺, m/z 195 [Cl₄-BaP]⁺⁺, m/z 159 [Cl₄-BaP-2HCl]⁺⁺, m/z 141[Cl₂-BaP-HCl]⁺⁺.

Combustion of polystyrene in an air/Cl₂ atmosphere

179 mg (1,7 mmol) of polystyrene were burned in portions in a Heraeus vertical tube oven at 800°C under a flow (840 mL/min) of a air-chlorine mixture (mixture air/Cl₂: 4/1 and 9/1). The reacted gases were passed through 2 wash bottles in series, each cooled to -10°C, the first containing CCl₄ and the second CHCl₃ (Figure 1).

Clean up

The solutions in the wash bottles were then combined, and evaporated to dryness in a rotary evaporator under vacuum control, the solid burning product remaining was then redissolved in 2mL toluene and passed through 5g silicagel deactivated with 10% water (column diameter: 10 mm) with 15 mL hexane followed by 8 mL of a hexane-dichloromethane (hx-CH₂Cl₂) mixture (1:1) as eluent for purification. The hx-CH₂Cl₂ fraction was concentrated down to 500 µL, 1 µL of which was injected into the GC-MS.

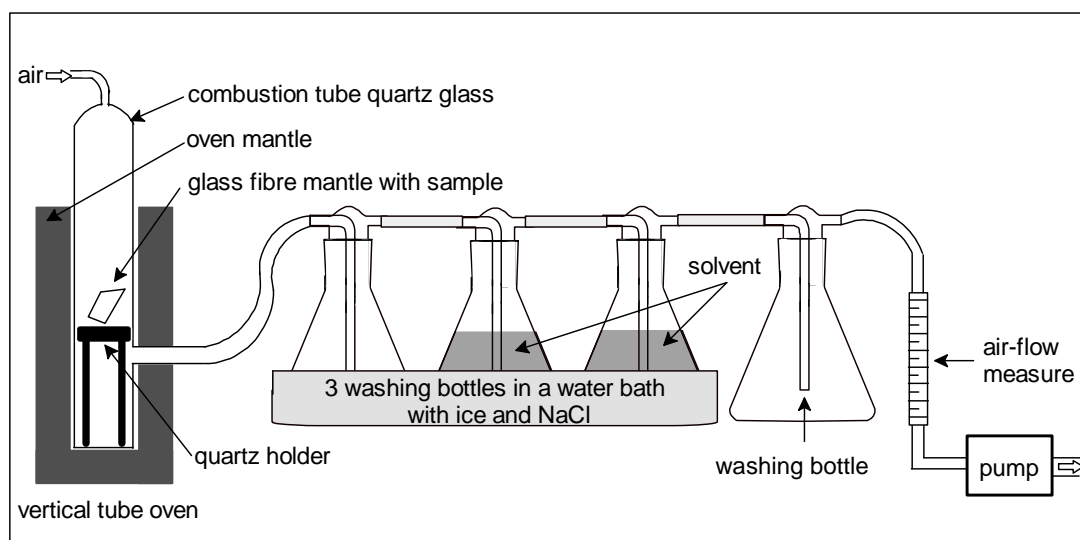


Figure 1: Experimental setup for the combustion of Polystyrene in the Heraeus vertical tube oven

GC-MS Analyses

GC-MS analyses were carried out on a HP 5890 Series II directly coupled to a MSD HP 5972A (transfer line temperature 310°C, EI 70 eV), using splitless (1 min) injection at 295°C onto a DB5ms J&W Scientific (20 m x 0,18 mm i.d.; 0,18 µm f.th.) fused silica capillary column and a constant He flow of 1 mL/min with the

following temperature programme: 90°C for 1 min; 30°C/min to 300°C. Detection limit of pure compound was 0,8 pg/μL (SIM), recovery for 7-Cl-BaP and 7,12-Cl₂-BaP >90%,

BaP (purity >97%) was obtained from Sigma-Aldrich. All other chemicals and solvents were p.a or pure grade and obtained from Merck; silicagel (0,032 – 0,063 mm) was obtained from Riedel de Haen.

Results and discussion

Synthesis of reference compounds from BaP by chlorination using chlorine dissolved in CCl₄ under various different conditions, gave high purity 6-Cl-BaP and 3,6-Cl₂-BaP and also Cl₃-BaP and Cl₄-BaP which, however, could only be obtained as preparatively inseparable isomeric mixtures. Although a second dichlorinated BaP was initially found in small amounts during the synthesis of 3,6-Cl₂-BaP, this could be suppressed by optimising there reaction conditions.

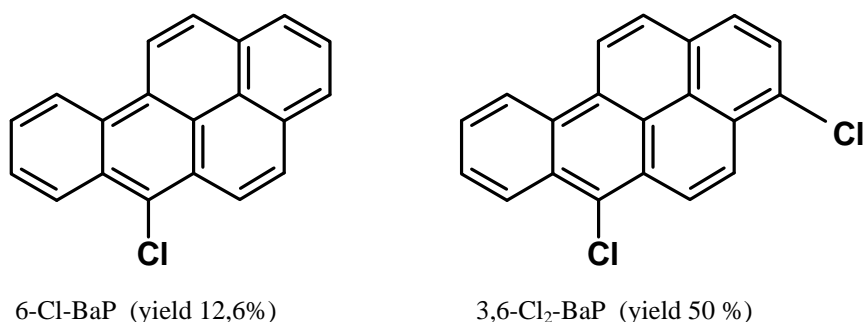


Figure 2: Yield and formula of synthesized chlorinated benzo[a]pyrenes

Incineration of BaP produced a large number of typical products, among others; chlorinated PAHs could be identified by GC-MS based on their TIC (figure 3) and mass spectra. Using the synthesized reference substances, 6-Cl-BaP and 3,6-Cl₂-BaP as well as isomers of Cl₃-BaP could be definitely identified and 6-Cl-BaP and 3,6-Cl₂-BaP quantified. Isomes of Cl₄-BaP in contrast were not seen. Table 1 shows the amounts of 6-Cl-BaP, 3,6-Cl₂-BaP and Cl₃-BaP obtained from BaP as well as conversion factors.

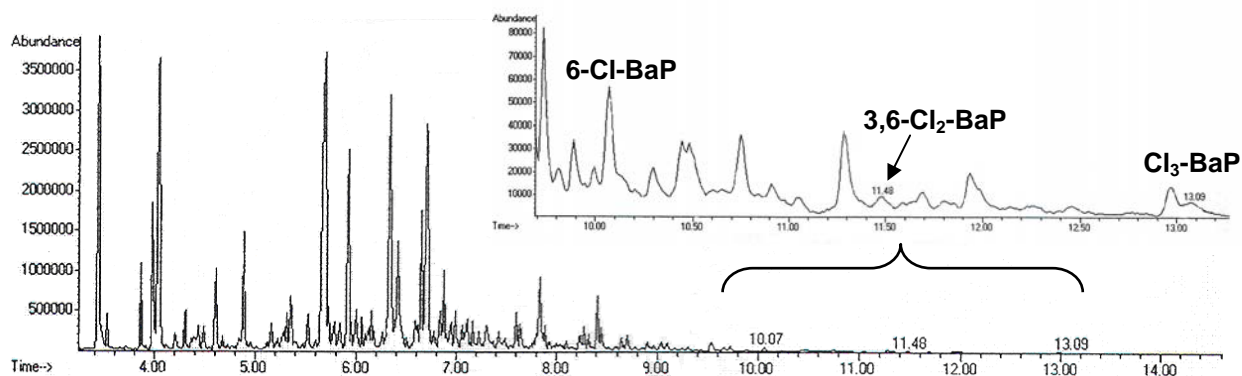


Figure 3: TIC of the combustion products of polystyrene incineration in air/Cl₂

For 6-Cl-BaP, 3,6-Cl₂-BaP and the isomers Cl₃-BaP the retention indices and relative retention times were measured (table 2).

Table 1: Produced amount of selected chlorinated BaPs by combustion of 179 mg BaP

| | amount [μg] | conversion factor |
|--------------------------|--------------------------|---------------------|
| 6-Cl-BaP | 2,8 | $1,6 \cdot 10^{-5}$ |
| 3,6-Cl ₂ -BaP | 0,6 | $3,4 \cdot 10^{-6}$ |
| Cl ₃ -BaP | 0,7 | $3,9 \cdot 10^{-6}$ |

Table 2: Retention index and relative retention time of selected chlorinated BaPs

| | retention index | rel. retention time |
|--------------------------|-----------------|---------------------|
| 6-Cl-BaP | 10,044 | 0,596 min |
| 3,6-Cl ₂ -BaP | 11,452 | 0,680 min |
| Cl ₃ -BaP | 13,047 | 0,775 min |

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