THIAARENES - THEIR ENVIRONMENTAL OCCURRENCE AND BIOLOGICAL ACTIVITY

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) are a well known class of carcinogenic pollutants in the human environment. Their biological potential and metabolism have been thoroughly investigated. Thiaarenes, i.e. sulfur-containing polycyclic aromatic compounds (S-PAC) deriving from thiophene, often are associated with PAH especially in crude oil and in hard coal emission and exhibit very similar chemical properties. However, little efforts have been made to study the environmental relevance and the metabolism of thiaarenes (1). More recently, evidence for the carcinogenic and mutagenic activities of some thiaarenes has been presented (2, 3) and there are also strong indications that they may contribute to the carcinogenic potential of environmental matter, for instance in case of emissions from hard coal combustion (4).

MATERIALS AND METHODS

Enrichment of S-PAC

During the enrichment procedure thiaarenes remain in the PAH-fraction from which they may be separated by an oxidation/reduction process or by adsorption to palladium chloride.

Figure 1: Scheme of PAH-enrichment from flue gas condendate

<table>
<thead>
<tr>
<th>Condensate</th>
<th>Me + water + (CH(7+3×10))</th>
<th>Me + water (I)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH</td>
<td>CH + NM (1×1)</td>
<td>CH (I)</td>
</tr>
<tr>
<td>NM</td>
<td>Sephadex LH20 / isopropanol</td>
<td></td>
</tr>
<tr>
<td>2-3 rings PAC (III)</td>
<td>4-7 rings PAC</td>
<td>polar PAC (IV) and &gt;7 rings PAH</td>
</tr>
<tr>
<td>Sephadex LH20 / Me-water-CH</td>
<td>4-7 rings PAH and S-PAC (III)</td>
<td>N-PAC and other polar (IV)</td>
</tr>
</tbody>
</table>

Figure 1: Scheme of PAH-enrichment from flue gas condendate

- CH = cyclohexane
- Me = methanol
- NM = nitromethane
- PAC = polycyclic aromatic compounds
- N-PAC = nitrogen-containing PAC
Metabolic Studies

The preparation of rat liver microsomes and the incubation conditions have been published elsewhere (5).

RESULTS

The PAH-profile of the emission from hard-coal fired furnaces exhibits a total number of at least 119 different individuals, about one third of which could be characterized as S-PAC when recorded by a sulfur-selective GC-detector and/or analyzed by mass spectrometry.

Studying the carcinogenic activity of hard-coal emission, it became evident that this activity is almost entirely caused by the PAH-fraction (4) (see Figure 2).

![Figure 2: Balance of the carcinogenic activity of the emission from coal-fired furnaces. Dosage: 0.411 mg condensate twice a week. Fractions were dosed proportionately.](image-url)

Further fractionation into a lower and a higher-boiling fraction evidenced that the carcinogenic potential is equally distributed to both fractions, i.e. that 4- and 5-ring systems on one hand, and 6 and more rings-containing systems on the other one, equally contribute to the carcinogenic activity of hard coal emission (4).

From various studies (3, 6) it is well known that the thiaarenes detected in environmental matter, are potent mutagens when activated by mammalian liver enzymes. We found that benzo(2,3)-phenanthro(4,5-bcd)-thiophene - an isoster to benzo(a)pyrene - exhibits an exceptional high mutagenic effect in Salmonella typhimurium TA98 und TA100 as well as in E. coli, being double as potent as benzo(a)pyrene itself (6). Although less efficient, other environmentally relevant thiaarenes were also found to be more or less potent mutagens.

Recently, Croisy et al. (7) tested some thiaarenes for carcinogenicity by subcutaneous injection into mice. A comparison to structurally related carbocyclic isosters shows that the thiaarenes in those cases investigated were more potent carcinogens than the PAH (Figure 3).