Gas-Chromatographic Analysis of Organic Compounds Formed in Avalanches Around Wires

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Aim

• to analyse stable organic compounds formed in electron avalanches in a proportional counter filled with Ar/ethylene gas mixture.

• previous surveys:
  
Content

- Description on the gas analysis system and its operation and limitations.
- Analysis of compounds.
- Production of compounds with different irradiation rate.
Detector

- single wire proportional counter
  - gold plated Cu-Be wire (25 µm)
  - other parts: stainless steel, PTFE
  - aluminised Mylar window (clued by Epotek epoxy)
- gas: Ar/C\textsubscript{2}H\textsubscript{4} 50/50
- temperature: 50 - 70 °C
- gas amplification ~2 x 10\textsuperscript{4}
- irradiation by X-ray tube (Cu target)
- anode current 10 - 500 nA
Irradiation test bench for ageing studies of gas filled radiation detectors
Gas analysis system for ageing studies of gaseous radiation detectors

- Sample concentration by cryotrap (for heavier compounds than quenching gas)
- Tandem gas chromatograph: first GC for quantitative analysis, second GC-MS for identification
- For analysis of organic compounds formed in electron avalanches or outgassed from detector materials
Trapping sequences

I Phase  Purge / Cooling

II Phase  Sample Trapping

III Phase  Sample Injection to GC
Timing diagram of cryotrapping

Purge

Cooling

Sample collecting

Warming

Sample transfer

GC run
Trap temperature and sample flow during trapping

![Graph showing trap temperature and sample flow over time. The graph displays two separate lines: one for trap temperature in °C, which remains relatively constant around -85°C, and another for sample flow in ml/min, which fluctuates around 0 ml/min. The x-axis represents time in seconds, ranging from 0 to 1800 s.]
Limitations of system

• detects just stable organic compounds heavier than quenching gas.
• detector in elevated temperature.
• sensitivity ~ 1 ng (depends in trapping time and compounds).
• complicated and time consuming operation.
Gas chromatogram of compounds observed in a proportional counter filled with Ar/C₂H₄ 50/50 gas mixture.
Some identified compounds created in electron avalanches in proportional mode with Ar/C₂H₄ 50/50 gas mixture.
Avalanche compounds identified

<table>
<thead>
<tr>
<th>PEAK</th>
<th>COMPOUND</th>
<th>SOURCE</th>
<th>REMARK</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Asetaldehyde</td>
<td>Electron aval.</td>
<td>Polymerising improbable.</td>
</tr>
<tr>
<td>2</td>
<td>1,3-butadiyne</td>
<td>Electron aval.</td>
<td>Explosively polymerising.*</td>
</tr>
<tr>
<td>3</td>
<td>Ethanol</td>
<td>Electron aval.</td>
<td>Polymerising improbable.</td>
</tr>
<tr>
<td>4</td>
<td>1,3-pentadiene</td>
<td>Electron aval.</td>
<td>Able to polymerise.</td>
</tr>
<tr>
<td>5</td>
<td>2-methyl-2-propanol</td>
<td>Electron aval.</td>
<td>Polymerising improbable.</td>
</tr>
<tr>
<td>7</td>
<td>2-ethoxy-2-methylpropane</td>
<td>From system.</td>
<td>Polymerising improbable.</td>
</tr>
<tr>
<td>8</td>
<td>2-methyl-1,3-dioxolane</td>
<td>Electron aval.</td>
<td>Polymerising improbable.</td>
</tr>
<tr>
<td>9</td>
<td>2-methoxy-ethanol</td>
<td>Electron aval.</td>
<td>Polymerising improbable.</td>
</tr>
<tr>
<td>10</td>
<td>1,3-hexadien-5-yne</td>
<td>Electron aval.</td>
<td>Able to polymerise.</td>
</tr>
<tr>
<td>11</td>
<td>3-methyl-1,3-pentadiene</td>
<td>Electron aval.</td>
<td>Able to polymerise.</td>
</tr>
<tr>
<td>12</td>
<td>4-methyl-1,4-hexadiene</td>
<td>Electron aval.</td>
<td>Able to polymerise.</td>
</tr>
<tr>
<td>13</td>
<td>2,4-heptadiene</td>
<td>Electron aval.</td>
<td>Able to polymerise.</td>
</tr>
<tr>
<td>14</td>
<td>Tetrachloroethylene</td>
<td>From gas bottle.</td>
<td>Contaminant in ethylene bottle.</td>
</tr>
<tr>
<td>15</td>
<td>1-ethenyl-4-ethylbenzene</td>
<td>Electron aval.</td>
<td>Able to polymerising.</td>
</tr>
<tr>
<td>16</td>
<td>2,3-dihydro-1-methylindene</td>
<td>Electron aval.</td>
<td>Polymerising improbable.</td>
</tr>
<tr>
<td>17</td>
<td>4-ethylbenzaldehyde</td>
<td>Electron aval.</td>
<td>Polymerising improbable.</td>
</tr>
</tbody>
</table>

* “Potentially very explosive, it may be handled and transferred by low temperature distillation. It should be stored at -25 °C to prevent decomposition and formation of explosive polymers.” (Armitage, J.B. et al., J.Chem.Soc., 1951, 44)
Ethylene + water

\[ 2 \text{CH}_2=\text{CH}_2 + 2\text{H}_2\text{O} \rightarrow 2 \text{CH}_3\text{CH}_2\text{OH} \quad \text{ethanol (peak 3)} \]

\[ 2 \text{CH}_2=\text{CH}_2 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{C} - \text{C} - \text{CH}_3 \quad 2\text{-methyl-2-propanol (peak 5)} \]

\[ 3 \text{CH}_2=\text{CH}_2 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{C} - \text{C} - \text{CH}_3 \quad 2\text{-ethoxy-2-methyl-propane (peak 7)} \]

(or by secondary reactions:

\[ \text{H}_3\text{C} - \text{C} - \text{CH}_3 + \text{CH}_3\text{CH}_2\text{OH} \rightleftharpoons \rightleftharpoons \text{H}_2\text{O} + \text{H}_3\text{C} - \text{C} - \text{CH}_3 \quad \text{Impurity from system} \]
Ethylene + Oxygen

\[ 2 \text{CH}_2=\text{CH}_2 + \text{O}_2 \rightarrow 2 \text{CH}_3\text{CHO} \text{ (asetaldehyde)} \] (peak 1)

\[ 2 \text{CH}_2=\text{CH}_2 + \text{O}_2 \rightarrow \text{H}_3\text{C}-\text{O}-\text{CH}_2-\text{CHO} + :\text{CH}_2 \text{ (peak 6)} \]

methoxy-asetaldehyde (+carbene radical react further)

\[ 2 \text{CH}_2=\text{CH}_2 + \text{O}_2 \rightarrow 2\text{-methyl-1,3-dioxolane} \text{ (peak 8)} \]

\[ 2 \text{CH}_2=\text{CH}_2 + \text{O}_2 \rightarrow \text{CH}_3\text{-O-CH}_2\text{-CH}_2\text{-OH} + \text{C} \text{ (peak 9)} \]

2-methoxy-ethanol

( or by secondary reactions:)

\[ \text{CH}_4+\frac{1}{2}\text{O}_2+\text{CH}_3\text{-CH}_2\text{-OH} \rightarrow \rightarrow \text{CH}_3\text{-O-CH}_2\text{-CH}_2\text{-OH} + \text{H}_2 \]

\[ \text{CH}_3\text{OH} + \text{CH}_3\text{-CH}_2\text{-OH} \rightarrow \rightarrow \text{CH}_3\text{-O-CH}_2\text{-CH}_2\text{-OH} + \text{H}_2 \]
Aromatic hydrocarbons

\[ 5 \text{CH}_2=\text{CH}_2 \rightarrow 4 \text{H}_2 + \text{H}_3\text{CCH}_2\text{C}_{\text{CH}}\text{CH}_2 \]

1-ethenyl-4-ethyl-benzene (peak 15)

\[ 5 \text{CH}_2=\text{CH}_2 \rightarrow 4 \text{H}_2 + \text{CH}_3\text{H}\text{C}_{\text{H}}\text{H}_3\text{CCH}_2\text{C}_{\text{CH}}\text{CH}_2 \]

2,3-dihydro-1-methylindene (peak 16)

\[ 10 \text{CH}_2=\text{CH}_2 + \text{O}_2 \rightarrow 2\text{CH}_4 + 6\text{H}_2 + 2 \text{H}_3\text{CCH}_2\text{C}_{\text{CH}}\text{CH}_2 \]

4-ethyl-benzaldehyde (peak 17)
Aliphatic hydrocarbons
(Initial chaining?)

2 \( \text{CH}_2 = \text{CH}_2 \rightarrow \rightarrow \text{HC} \equiv \text{C-C} \equiv \text{CH} + 3 \text{H}_2 \) 1,3-butadiyne (Peak 2)

3 \( \text{CH}_2 = \text{CH}_2 \rightarrow \rightarrow \text{CH}_2 = \text{CH-CH} = \text{CH-CH}_3 + \text{CH}_4 \) 1,3-pentadiene (Peak 4)

3 \( \text{CH}_2 = \text{CH}_2 \rightarrow \rightarrow \text{CH}_2 = \text{CH-CH} = \text{CH-C} \equiv \text{CH} + 3\text{H}_2 \) 1,3-hexadien-5-yne (Peak 10)

3 \( \text{CH}_2 = \text{CH}_2 \rightarrow \rightarrow \text{CH}_2 = \text{CH-C(-CH}_3\text{)} = \text{CH-CH}_3 + \text{H}_2 \) 3-methyl-1,3-pentadiene (Peak 11)

4 \( \text{CH}_2 = \text{CH}_2 \rightarrow \rightarrow \text{CH}_2 = \text{CH-CH}_2\text{-C(-CH}_3\text{)} = \text{CH-CH}_3 + \text{CH}_4 \) 4-methyl-1,4-hexadiene (Peak 12)

4 \( \text{CH}_2 = \text{CH}_2 \rightarrow \rightarrow \text{CH}_3\text{-CH} = \text{CH-CH} = \text{CH-CH}_2\text{-CH}_3 + \text{CH}_4 \) 2,4-heptadiene (Peak 13)
Rate dependence of production of avalanche compounds
(Ar/C₂H₄ 50/50)

constant total charge
0.1 mC

Peak area vs. rate [mC/h]

1,3-pentadiene (CH₂=CH-CH=CH-CH₃)
asetaldihyde (CH₃CHO)

165 min
10 nA
5 min
320 nA
Remark for accelerated aging tests

• in accelerated aging tests irradiation rates are increased by factor of several hundreds.
• molarity should be taken into account for those impurity compounds which are supposed to react with avalanche compounds.

\[
\begin{align*}
A + I & \rightarrow C \\
B + I & \rightarrow D
\end{align*}
\]
Summary

• Some organic compounds formed in electron avalanches in Ar/C\textsubscript{2}H\textsubscript{4} 50/50 gas mixture analysed and identified.

Future

• effect of O\textsubscript{2}
• effect of additives and outgassing components.
• new gas mixtures (P-10)