Analysis of organic compounds formed in electron avalanches in a proportional counter filled with Ar/C_2H_4 gas mixture

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Abstract

Some organic chemical compounds formed in electron avalanches have been analyzed by using a tandem gas chromatograph equipped with a cryogenic sample concentration unit. The characteristics of the analyzer are described. Fifteen stable compounds created in a proportional counter filled with Ar/C_2H_4 50/50 gas mixture were identified. Several compounds containing double or even triple bonds were found. Some potential reactions leading to production of the compounds are shown. Production rates of two compounds were observed to depend on the irradiation rate.

Keywords: Aging; Plasma chemistry; GC-MS analysis

1. Introduction

A large number of organic compounds and radicals are involved in the radiation-induced plasma chemical processes occurring in gaseous detectors. Some of these reactions produce large molecular chains forming polymer structures on anode or cathode surfaces. Identification of the organic compounds produced in electron avalanches may help us to understand the basic chemical processes causing these aging effects.

Numerous studies have analyzed the gas compositions in wire chambers and their impurities, and in some studies, the wire deposits have been identified as well. However, few surveys have investigated the stable compounds created in the plasma chemical reactions of proportional mode in gaseous detectors [1,2], and, to the best of our knowledge, no research has analyzed the radicals of electron avalanches in proportional mode.

We present here an analysis of organic compounds formed in electron avalanches in a proportional counter filled with an Ar/ethylene 50/50 gas mixture and irradiated with soft X-rays.

2. Experimental setup

2.1. Detector

The detector under study was a single-wire proportional counter consisting of a stainless steel cathode, PTFE end plugs, a gold-plated tungsten wire (diameter 25 microns), and a thin aluminized Mylar window glued by EPOTEK 377 epoxy. The fill gas was Ar/C_2H_4 in a 50/50-mixture. The detector and gas tubes

downstream were heated (60 - 100 °C) to prevent condensation of the compounds before the analyzer. The temperatures of the detector and of the gas tubing were controlled during the analysis.

The detector was irradiated by an X-ray tube (Cu target) with variable rates. The detector bias was chosen so that the gas amplification was of the order of 10^4 as measured with a weak [55]Fe 5.9 keV X-ray source (Fig. 1). The operation mode was hence well in the proportional region, at least at low irradiation rates. Typical anode current during the irradiation was a few hundred nanoamps. The anode current of the detector was monitored with a precision of 1 nA, and the collected total charge was calculated by integrating over the measured current values.

2.2. Gas analysis system

The gas analysis system, shown in Figure 2, consisted of a cryogenic sample concentration unit (a cryotrap) and two gas chromatographs (GC) in a tandem configuration [3]. The first GC (DANI 86.10HT) utilized a GS-Q PLOT column and a FID detector sensitive to organic compounds. The latter (HP GCD) was equipped with an HP-5 column and a quadruple mass spectrometer. At the end of the GS-Q PLOT column, was a tee adapter, in which the sample was separated into two lines: one part into the FID detector (20% of the sample) and the rest into the Valco® 8-path valve. The arrangement ensured a sufficient sample for identification of the compounds by HP GCD. The HP GCD was provided with a loop tube (6 meters long, 1/16″ diameter) for sample collection in the Valco® 8-path valve. The sample was injected by a helium carrier gas to the column through a deactivated silica capillary joint.

The outflow from the proportional counter was fed through a heated sample valve into the cryotrap. The trapping procedure contained three phases, as shown in Figure 3: 1) purging the trap and cooling it down to the operation temperature; 2) sample trapping (5 - 180 min); and 3) sample injection to the first GC by a quick heating of the cryotrap. Temperature control of the cryotrap was achieved by controlling a flow of gaseous nitrogen cooled by liquid nitrogen. A precise temperature control is essential to allow the organic quenching component of the gas mixture to pass the trap and to trap simultaneously those compounds whose boiling points are higher than that of the quenching gas.

The trapping efficiency as a function of the trap temperature was measured with the help of a calibration gas containing 1 ppm of hexane and isobutane in pure argon. The calibration gas was mixed with a small amount of ethylene, and peak areas of ethylene, hexane, and isobutane were measured in different temperatures of the trap (Fig. 4). The results indicated that the optimal temperature of the cryotrap was between -130 and -140°C. Then the hexane was fully trapped and the isobutane partly, whereas the major part of ethylene passed the trap without trapping. If the trap temperature was too low, the sample flow was blocked due to the increased condensation of the ethylene. For this reason, both the trap temperature and the sample flow were monitored during the sampling period.

The trapping efficiency as a function of a flow rate of the sample was measured as well (Fig. 5). The measurement indicated that the full trapping efficiency of hexane was retained at least to the flow rate of 50 ml/min, whereas for the isobutane the efficiency was lost already at a flow rate of a few ml/min (not shown in the figure). The deviation from linearity for hexane was within 5 %. The calculated mass of the hexane sample collected by the trap is also shown in the figure. The slope of the linear fit for this scale is 738 (ng)$^{-1}$. When the minimum peak area to be detected reliably in the actual analysis is around 1000, the sensitivity of the system for hexane may be estimated to be around 1 ng. A similar sensitivity was obtained for methanol by injecting a small amount of it into the gas flow.

The trapping efficiency as a function of the trapping time was also studied. The measurements were done both with a pure calibration gas and with a 50/50-mixture of calibration gas and ethylene. The latter was needed to check that the large amount of hydrocarbon in the gas mixture would not degrade the trapping efficiency. The results indicated a good linear dependence of efficiency versus trapping time in a time scale from 5 min up to 2.5 h, and no degradation in efficiency due to the hydrocarbon content was observed.

The repeatability of measurements was estimated by eight successive analyses of the

hexane concentration of the calibration gas. The maximum deviation from the average peak area was 3% and the overall standard deviation 2.2%.

2.3. Limitations of the system

Although the analysis system is shown to be capable of detecting and identifying organic compounds in a gas mixture of a proportional counter, the system has some limitations with respect to its usage in aging studies. For instance, only stable compounds are detected, not radicals. Only compounds having melting/boiling point higher than that of the quenching component are observed. The detector is operated at an elevated temperature, so some reactions are not necessarily the same as they would be at room temperature. The actual polymer deposition on cathode or anode surfaces is not seen due to the increased temperature, but merely the boiling products at best. (In fact, there is no sign of aging in the counter after collection of total charge of several hundreds of mC per wire centimeter.)

3. Results

Figure 6 shows a typical chromatogram of the gas analysis. More than 20 compounds were observed in addition to the ethylene peak and a couple of background peaks. The 15 most prominent peaks were identified and are listed in Table 1. Peaks are numbered according to Figure 6. In the last column is a rough estimation of the compound's tendency to form polymer chains (i.e., whether or not the compound has double or triple bonds).

Seven of these compounds were considered capable of polymerization. Two of them, 1,3-butadiyne and 1,3-hexadien-5-yne, even contained triple bonds, which can form molecular chains that still contain double bonds. These double bonds may open further and form crosslinking between the polymer chains, leading to very stable molecular structures. In fact, 1,3-butadiyne is known to form polymers explosively [4].

Several compounds listed in the table contain oxygen. The gas system, the detector, and the analyzer were examined by a leak tester, and no measurable leakage was detected. However, concentration of the compounds found is at ppb level, at which

scale water and oxygen are always present in ordinary gas systems.

Reactions between ethylene molecule(s) and water or oxygen may lead to production of many of these compounds. Production of the ethanol and the acetaldehyde are the basic forms of these type of reactions. Many of these compounds are also found among the known combustion products of the argon-ethylene gas mixture [5]. Production of the other compounds may be explained by mutual reactions of several ethylene molecules. Some potential reactions are listed in Table 2. Most of the reactions have several intermediate stages between the starting compounds and the final products. Therefore, the reactions should be viewed only as guidelines to what kind of and how many molecules are needed to form the final compounds, without paying attention to the actual reaction chains. The emergence of aromatic hydrocarbons in particular is likely more complex than the others.

Production of aliphatic hydrocarbons may be a sign of an initial chaining of the ethylene molecules. Four ethylene molecules are required to form the heaviest hydrocarbon observed.

4. Dependence of production of the compounds on the irradiation rate

In accelerated aging tests, a presumption is made that the chemical environment in electron avalanches is independent of the irradiation rate. Validity of this presumption was studied by measuring the production rate of the avalanche compounds as a function of the irradiation rate.

The irradiation rate of the X-ray device, and consequently the anode current of the proportional counter, was varied, and the irradiation (trapping) time was adjusted so that the total charge collected was retained in 0.1 mC in all the measurements. The irradiation time was varied from 5 min to 165 min, and the anode current from 320 nA to 10 nA, respectively. The peak areas of some of the compounds listed in Table 1 were measured. The results are shown in Figure 7.

The two most prominent peaks in the chromatograph (see Fig. 6), acetaldehyde and 1,3-pentadiene, were observed to depend inversely on the irradiation rate, whereas the

areas of most of the other peaks were more or less independent of the irradiation rate. The 1,3-pentadiene is the second lightest compound able to polymerize. It is evidently an intermediate product and a building block for the heavier hydrocarbons observed (see Table 2). Its consumption in a higher-irradiation environment may hence be larger than at a lower irradiation rate. The concentration of the lightest compound, 1,3-butadiyne, is not high enough to enable reliable comparison of the production rates at different irradiation rates.

5. Remark for accelerated aging tests

It is important to note that not all the chemical reactions are necessarily scalable in the accelerated aging tests. In the accelerated aging tests, irradiation is increased by some factor (F) to expose the detector in a short period of time to the same amount of radiation that it would collect during the actual experiment, which would last perhaps several years. Let's suppose that in an accelerated aging test, an effect of some impurity will be studied through the deliberate addition of a small amount of it to the gas mixture. If this impurity were to react with a compound created in the avalanche, it would be necessary to increase its concentration also by factor F in the test to ensure that the same molar quantity would be available for the reaction as in the real experiment. However, the other reactions the impurity compound may have with compounds not formed in the electron avalanches may then be erroneously enhanced due to the excess amount of the impurity in the gas mixture. This reasoning is not valid for those impurities and additives that are found in large quantities in the gas mixture and are not acting as a limiting component in the reactions mentioned above.

6. Conclusion

The gas analysis system described is shown to be able to analyse and identify several organic compounds created in electron avalanches of a proportional counter. Several compounds containing double or triple bonds, and hence potentially able to polymerize, were observed to be produced in Ar/C_2H_4 gas mixture. Production rates of two compounds were found to increase with a decreasing irradiation rate.

References

[1] J. Wise, et al., IEEE Trans. Nucl. Sci. NS-35 (2) (1990) 470.
[2] J. Kadyk, Nucl. Instr. and Meth. A 300 (1991) 436.
[3] K. Kurvinen, J. Ojala, T. Särme, Nucl. Instr. and Meth. A 461 (2001) 88.
[4] J.B.Armitage, et al., J. Chem. Soc. (1951), 44.
[5] N.Olten, S.M. Senkan, Formation of polyaromatic Hydrocarbons in an Atmospheric Ethylene Diffusion Flame, submitted to "The 27th International Symposium on Combustion".

Figure captions:

Fig. 1.   A gas amplification of the proportional counter filled with Ar/C_2H_4 50/50-gas mixture versus detector bias voltage. The measurements were done in two different temperatures (30°C and 100°C) and in slightly different atmospheric pressures.

Fig. 2.   A tandem gas chromatograph system equipped with a cryogenic sampling unit and with a mass spectrometer.

Fig. 3.   The sample and carrier gas flows during the trapping sequences; a) a purge and cooling phase, b) the sample trapping and c) a sample transfer and injection to the first gas chromatograph.

Fig. 4.   Peak areas of ethylene, isobutane and hexane in different trapping temperatures measured from a gas mixture containing calibration gas (1 ppm hexane and isobutane in argon) and a small amount of ethylene.

Fig. 5.   Peak areas of the hexane of the calibration gas as function of the sample flow rate. The sample flow is converted also to a mass of hexane and represented on the secondary horizontal axis along the sample flow.

Fig. 6.   A gas chromatogram of an analysis of stable organic compounds originating from electron avalanches in a proportional counter filled with Ar/C_2H_4 50/50-gas mixture. The trapping time was 30 min, collected charge 0.5 mC and the sample flow rate 10 ml/min. The dashed line shows the background peaks, when the X-ray irradiation was switched off. The vertical scale is slightly shifted for clarity. The compounds corresponding the peaks are listed in Table 1.

Fig. 7.   Peak areas of some peaks shown in Fig. 6 as a function of irradiation rate of X-rays (indicated as a charge collected from the detector within a period of time). The collected total charge was kept constant (0.1 mC) in all the measurements by adjusting the trapping time accordingly.

Table 1.   Compounds found from electron avalanches in a proportional counter filled with Ar/C_2H_4 50/50-gas mixture. The peak numbers refer to the gas chromatogram in Fig. 6.

PEAK	COMPOUND	SOURCE	REMARK
1	Acetaldehyde	Electron aval.	Polymerising improbable.
2	1,3-butadiyne	Electron aval.	Explosively polymerising.
3	Ethanol	Electron aval.	Polymerising improbable.
4	1,3-pentadiene	Electron aval.	Able to polymerise.
5	2-methyl-2-propanol	Electron aval.	Polymerising improbable.
6	Methoxy-acetaldehyde	Electron aval.	Polymerising improbable.
7	2-ethoxy-2-methylpropane	From system.	Polymerising improbable.
8	2-methyl-1,3-dioxolane	Electron aval.	Polymerising improbable.
9	2-methoxy-ethanol	Electron aval.	Polymerising improbable.
10	1,3-hexadien-5-yne	Electron aval.	Able to polymerise.
11	3-methyl-1,3-pentadiene	Electron aval.	Able to polymerise.
12	4-methyl-1,4-hexadiene	Electron aval.	Able to polymerise.
13	2,4-heptadiene	Electron aval.	Able to polymerise.
14	Tetracloroethylene	From gas syst.	Contaminant in ethylene.
15	1-ethenyl-4-ethylbenzene	(Electron aval.)	Able to polymerise.
16	2,3-dihydro-1-methylindene	(Electron aval.)	Polymerising improbable.
17	4-ethylbenzaldehyde	(Electron aval.)	Polymerising improbable.

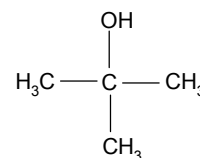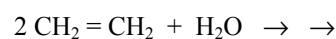**Table 2**   Potential reactions forming compounds observed in Fig.6.
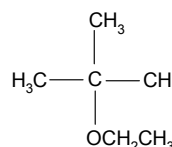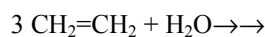
I Ethylene + water reactions

ethanol (<u>peak 3</u>): $2\ CH_2 = CH_2\ +\ 2H_2O\ \rightarrow\ 2\ CH_3CH_2OH$
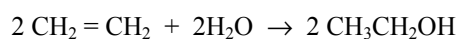
2-methyl-2-propanol (<u>peak 5</u>): $2\ CH_2 = CH_2\ +\ H_2O\ \rightarrow\ \rightarrow$

2-ethoxy-2-methyl-propane (<u>peak 7</u>): $3\ CH_2{=}CH_2 + H_2O \rightarrow \rightarrow$
(impurity from system)

or by secondary reactions:

$+CH_3CH_2OH$ $\leftrightarrow H_2O+$
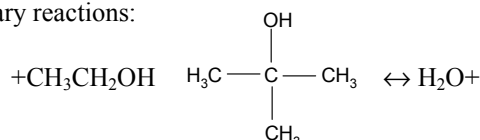
II Ethylene + oxygen reactions

acetaldehyde (<u>peak 1</u>): $2\ CH_2 = CH_2 + O_2\ \rightarrow\ 2\ CH_3CHO$

ethoxy-acetaldehyde (<u>peak 6</u>): $2\ CH_2 = CH_2 + O_2 \rightarrow \rightarrow H_3C\text{-}O\text{-}CH_2\text{-}CHO+{:}CH_2$
(carbene radical reacts further)
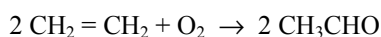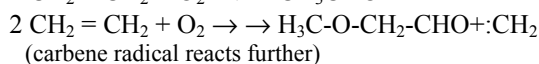
2-methyl-1,3-dioxolane (<u>peak 8</u>): $2\ CH_2 = CH_2 + O_2\ \rightarrow\ \rightarrow$

2-methoxy-ethanol (<u>peak 9</u>): $2\ CH_2 = CH_2 + O_2 \rightarrow \rightarrow CH_3\text{-}O\text{-}CH_2\text{-}CH_2\text{-}OH + C$
(or by secondary reactions:
$CH_4 + \frac{1}{2}O_2 + CH_3\text{-}CH_2\text{-}OH \rightarrow \rightarrow CH_3\text{-}O\text{-}CH_2\text{-}CH_2\text{-}OH + H_2$
$CH_3OH + CH_3\text{-}CH_2\text{-}OH \rightarrow \rightarrow CH_3\text{-}O\text{-}CH_2\text{-}CH_2\text{-}OH + H_2$).
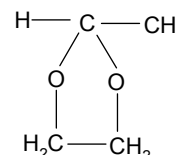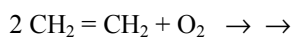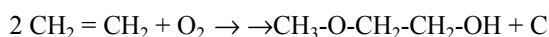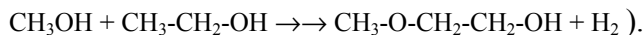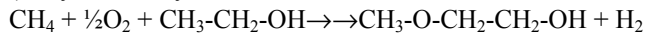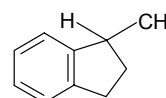
III Production of aromatic hydrocarbons

1-ethenyl-4-ethyl-benzene (<u>peak 15</u>): $5\ CH_2 = CH_2 \rightarrow \rightarrow 4H_2 +$
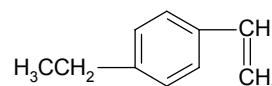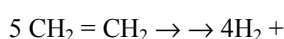
2,3-dihydro-1-methylindene (<u>peak 16</u>): $5\ CH_2 = CH_2 \rightarrow \rightarrow 4H_2+$
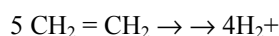
4-ethyl-benzaldehyde (<u>peak 17</u>): $10\ CH_2{=}CH_2+O_2 \rightarrow \rightarrow 2CH_4+6H_2+2$
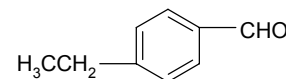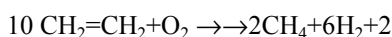
IV Production of aliphatic hydrocarbons

1,3-butadiyne (<u>peak 2</u>): $2\ CH_2 = CH_2 \rightarrow \rightarrow HC \equiv C\text{-}C \equiv CH + 3\ H_2$

1,3-pentadiene (<u>peak 4</u>): $3\ CH_2 = CH_2 \rightarrow \rightarrow CH_2 = CH\text{-}CH = CH\text{-}CH_3 + CH_4$
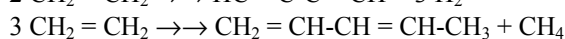
1,3-hexadien-5-yne (<u>peak 10</u>): $3\ CH_2 = CH_2 \rightarrow \rightarrow CH_2 = CH\text{-}CH = CH\text{-}C \equiv CH + 3H_2$

3-methyl-1,3-pentadiene (<u>peak 11</u>): $3\ CH_2 = CH_2 \rightarrow \rightarrow CH_2 = CH\text{-}C(\text{-}CH_3) = CH\text{-}CH_3 + H_2$
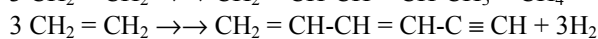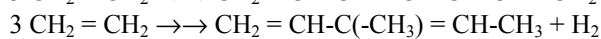
4-methyl-1,4-hexadiene (<u>peak 12</u>): $4\ CH_2 = CH_2 \rightarrow \rightarrow CH_2{=}CH\text{-}CH_2\text{-}C(\text{-}CH_3){=}CH\text{-}CH_3 + CH_4$

2,4-heptadiene (<u>peak 13</u>): $4\ CH_2 = CH_2\ \rightarrow \rightarrow CH_3\text{-}CH{=}CH\text{-}CH{=}CH\text{-}CH_2\text{-}CH_3 + CH_4$

Ar:C$_2$H$_4$ 50:50

100°C
1001 hPa

30°C
996 hPa

gas amplification
HV [kV]

a)
Sample valve
sample
Carrier gas
Trap tube
vent valve
pneumatic injection valve
GC
vent valve

b)
Sample valve
sample
Carrier gas
Trap tube
vent valve
pneumatic injection valve
GC
vent valve

c)
Sample valve
sample
Carrier gas
Trap tube
vent valve
pneumatic injection valve
GC
vent valve

peak area
sample flow [ml/min]
sample mass [ng]

isobutane
hexane
ethylene
peak area
trap temperature [°C]

ethylene
retention time [min]

constant total charge
0.1 mC
acetaldehyde (CH$_3$CHO)
peak area
rate [mC/h]