

ANALYSIS OF A COMPLEX GASEOUS MIXTURE BY TG-MS AND TG-FTIR

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Abstract

The thermal decomposition of sodium ethyl xanthate (SEX) was used to compare the techniques of pyrolysis-gas chromatography-mass spectrometry (py-GC-MS), thermogravimetry-Fourier transform infrared spectroscopy (TG-FTIR), and TG-MS.

In the py-GC-MS analysis, SEX was pyrolysed at 400°C in an inert atmosphere. Major gases evolved were carbon disulfide, diethyl sulfide, ethanol, and carbonyl sulfide. The TG of SEX exhibited a sharp mass loss at 201°C (42.3%) and a gradual mass loss at 217-325°C (20.8%). The MS spectra of the evolved gases were complex due to overlapping of molecular, isotope, and fragment ion signals. Using the MS in selected ion monitoring mode, the major gases evolved were found to be carbon disulfide and carbonyl sulfide. The FTIR spectra of the evolved gases displayed vibrational frequencies due to alkanes, carbonyls, carbonyl sulfide, and carbon disulfide.

From the analyses it was concluded that py-GC-MS provided unambiguous gas identification. Interpretation of the MS results was reliant on the py-GC-MS results, and the FTIR data was limited to identifying gases with very characteristic vibration frequencies.

Keywords: evolved gas analysis, FTIR, MS, pyrolysis-GC-MS, thermogravimetry

Introduction

Thermogravimetry (TG), when coupled with evolved gas analysis (EGA) techniques such as MS and FTIR, can provide useful information on determining the reaction(s) undergone during the decomposition of a material [1]. While TG-MS is considered as the most sensitive and versatile technique, TG-FTIR is more selective [2].

If these EGA techniques are used to study a material that decomposes into a few gases, identification of those gases is relatively simple. However, if a material decomposes into multiple gases, a number of problems arise [2]. Of these, the most significant problem is the overlap of signals from different gases, preventing identification as well as quantification. For complex gas mixtures, a separation step must be used if identification of specific evolved gases is required. The most popular system is gas chromatography-mass spectrometry (GC-MS). Such methods can be either off-line, in which the evolved gases are bubbled through a solvent or into an absorbent and then injected onto a GC-MS; or on-line where the TG apparatus is coupled

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directly to a GC-MS [3]. Another technique that could be used is pyrolysis-gas chromatography-mass spectrometry (py-GC-MS). Most pyrolysis units operate by heating the sample rapidly from ambient to a set temperature, although some pyrolysis units are temperature programmable. In the later mode the py-GC-MS system is closest to the experimental conditions used in TG-GC-MS.

Activated carbon is widely used in the gold processing industry as a means of adsorbing and thus separating gold cyanide ions from other species in solution. SEX is used as flotation reagent in the gold processing industry, but it can also adsorb onto activated carbon, which reduces its efficiency for gold adsorption. Thermal regeneration of the carbon is used to remove the SEX and any other compounds. Therefore if the thermal decomposition gases of SEX are known, it is possible to determine if the SEX has adsorbed on the carbon and if the regeneration was efficient [4]. Previous studies of SEX have found the gaseous decomposition products to be dioxanthenes, alcohols, elemental sulfur, dialkyl xanthates, thiols, carbonyl sulfide, carbon disulfide, hydrogen sulfide, and metallic sulfides [5].

The first objective of this paper is to compare TG-MS and TG-FTIR when used to study a material that decomposes into a complex gaseous mixture. SEX was chosen for this role. The second objective is to assess the possibility of using py-GC-MS to identify those gases.

Experimental

SEX was obtained from Hoechst chemicals, recrystallized [5], and kept in a desiccator. An elemental analysis combined with NMR and FTIR analyses confirmed the sample was SEX.

The py-GC-MS analysis was performed with a Pyrojector microfurnace (SGE Scientific) interfaced via a capillary inlet system to a Hewlett Packard 5809A gas chromatograph fitted with a 50 m \times 0.25 mm i.d. WCOT fused-silica cross-linked methylsilicone phase column (BP-1, film thickness 0.22 μ m, Hewlett Packard). The SEX sample was diluted with ten times its mass of quartz. A pellet of this diluted sample was introduced directly into the pyrolyser maintained at 400°C. Helium was used as both pyrolysis and carrier gas (linear velocity 60 cm s⁻¹), and injections were split approximately 25:1.

Thermal analysis experiments were performed using a Netzsch STA-409 instrument fitted with a TG sample carrier and interfaced via a heated transfer line (at 200°C) to either a Bruker IFS 55 FTIR spectrometer fitted with a MCT (HG-Cd-Te) detector, or to a Balzers Thermostar quadrupole mass spectrometer.

All analyses were performed in duplicate.

Results and discussion

py-GC-MS analysis

The gases identified from the pyrolysis of SEX at 400°C in an inert atmosphere are presented in Table 1 along with their retention time, abundance, and molecular mass. The evolved gases were identified using a mass spectra database.

Table 1 Gases evolved from the py-GC-MS analysis of SEX pyrolysed at 400°C

Retention/ min	Abundance/ %	Gas evolved	Molecular mass
1.64	1.34	hydrogen sulfide	34
1.78	11.0	carbonyl sulfide	60
5.13	17.5	ethanol	46
6.02	7.82	ethanethiol	62
6.82	0.30	diethyl oxide	74
7.32	28.2	carbon disulfide	76
16.8	21.5	diethyl sulfide	90
21.3	5.02	diethyl carbonate	118
28.0	1.18	diethyl disulfide	122
28.7	3.80	carbonothioic acid, O, S, diethyl ester	134
33.9	0.39	diethylthio methane	136
36.7	1.89	carbonodithioic acid O, S, diethyl ester	150

The pyrolysis produced 12 gases, of which carbon disulfide was the most abundant gas. Diethyl sulfide, ethanol, and carbonyl sulfide were also high in abundance. All other gases were considered as minor products. The pyrolysis of a less pure sample has been reported previously [4]. Nine of the gases are common between the two studies, but the current study found another three gases, that is diethyl oxide, carbonothioic acid, O, S, diethyl ester, and diethylthio methane. These extra gases were probably due to a higher purity SEX and slightly different py-GC-MS conditions.

TG analysis

The TG curve of SEX heated at $10^{\circ}\text{C min}^{-1}$ in a nitrogen atmosphere is presented with the MS and FTIR data in Figs 1 and 2. The TG curve showed two distinct mass losses. The first mass loss of 42.3% was rapid occurring between 169 and 217°C. The second mass loss of 20.8% was gradual occurring between 217 and 325°C.

MS analysis of the evolved gases

The evolved gases were initially studied by recording the mass spectrum from 10–300 amu (attenuated mass unit) for every 10°C increase, from ambient to 500°C. The mass spectra recorded were complex consisting of numerous peaks. The peaks were attributed to molecular, fragment, and isotope ions of numerous gases. The molecular ion peaks were identified using the py-GC-MS data, and the other peaks were assumed to be due to fragment and/or isotope ions.

The evolved gases were then studied by selected ion monitoring (SIM). The SIM program was set to monitor the molecular ions of the evolved gases from ambient to

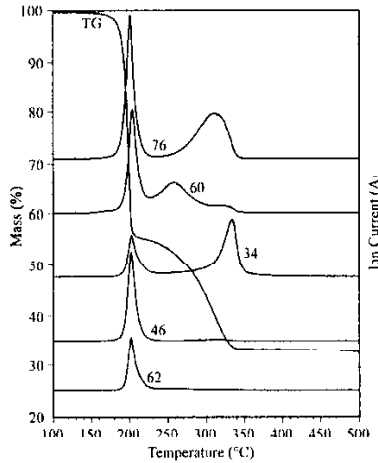


Fig. 1 Ion chromatograms of the evolved gases of SEX heated at $10^{\circ}\text{C min}^{-1}$ in a nitrogen atmosphere (Note: amu 76 has been reduced by a factor of 3)

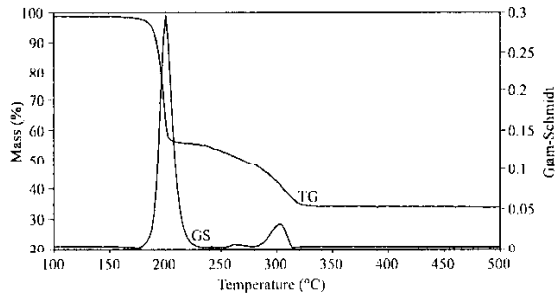


Fig. 2 TG-GS curves of SEX heated at $10^{\circ}\text{C min}^{-1}$ in nitrogen

500°C. Ion chromatograms were produced for each evolved gas. Using the ion chromatograms the abundance of the gases for each mass loss were calculated. The ion chromatograms for the most abundant gases are presented in Fig. 1, and their percentage abundance are reported in Table 2.

Although Table 2 shows the abundance of the major gases (95% of the total gases evolved), there may be considerable error in the percentages reported. This is because fragment and/or isotope ion signals may overlap the molecular ion signals of the same amu, thereby contributing to the ion abundance. Unfortunately the extent of overlapping cannot be calculated. Thus in the discussion of the ion chromatograms and their abundance the overlapping due to fragment and/or isotope ion signals has been ignored for simplicity.

In the first mass loss all the gases evolved as sharp peaks and these coincided with the TG curve. The most abundant gas was carbon disulfide, followed by carbonyl sulfide, ethanol, ethanethiol, and then hydrogen sulfide. All other gases were

Table 2 Abundance of the major evolved gases from the TG-MS analysis of SEX heated at $10^{\circ}\text{C min}^{-1}$ in a nitrogen atmosphere

amu	Abundance/%			Gas evolved
	first mass loss	second mass loss	total mass loss	
34	2.50	5.60	8.10	hydrogen sulfide
46	5.64	0.77	6.41	ethanol
60	8.65	8.91	17.6	carbonyl sulfide
62	3.58	0.83	4.41	ethanethiol
76	26.7	32.0	58.7	carbon disulfide

considered minor and unimportant. During the second mass loss, the gases evolved over different temperature ranges. That is, the majority of carbonyl sulfide, ethanol, and ethanethiol evolved at 260°C , while the majority of carbon disulfide and hydrogen sulfide evolved at 315 and 335°C respectively.

It is worthwhile to note that correction of the molecular ion chromatograms for fragment ion and/or isotope ion signals may be possible by using reference spectra. However the reference spectra must be collected on the same mass spectrometer for accurate and reliable correction. This was not practical for the mass spectrometer used in this study. A rough correction was done using reference spectra from another instrument. This indicated that below amu 60 the fragment and/or isotope ion signals were very high, and above amu 60 they were low.

FTIR analysis of the evolved gases

A typical TG-GS (Gram-Schmidt) curve of SEX heated at $10^{\circ}\text{C min}^{-1}$ in a nitrogen atmosphere is presented in Fig. 2. The two mass losses on the TG curve coincided with two peaks on the GS curve.

The infrared spectra of the two mass losses are presented in Fig. 3. Identification of the absorption bands was performed using characteristic infrared absorption wavelengths. The infrared spectrum of the first mass loss was complex due to the numerous absorption bands of many gases. Compounds that were identified as evolved gases were alkanes, carbonyls, carbonyl sulfide, and carbon disulfide. Carbonyl sulfide and carbon disulfide were the only gases detected in the second mass loss.

The absorption band at $3000\text{--}2800\text{ cm}^{-1}$ was associated with symmetric and asymmetric stretching of the C-H bond in methyl and methylene groups [6, 7]. This region indicated the presence of alkanes. At the $2100\text{--}2000\text{ cm}^{-1}$ absorption band there were two peaks. These peaks are due to the asymmetric and symmetric stretching of the carbonyl group contained in carbonyl sulfide [8-10]. The single 1760 cm^{-1} absorption band is in a region of the infrared spectrum which is characteristic for compounds containing a carbonyl group. There are also two peaks within the $1540\text{--}1520\text{ cm}^{-1}$ absorption band. These peaks are due to the asymmetric and symmetric

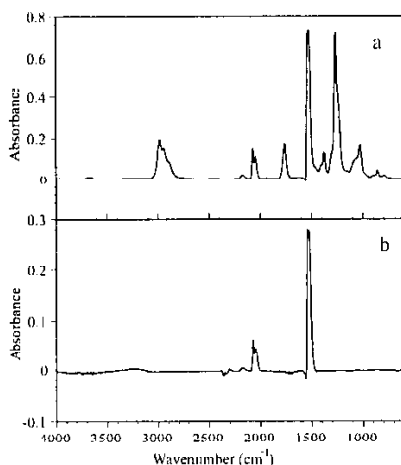


Fig. 3 Infrared spectra of the gases evolved from the two mass losses of SEX, a – first mass loss, b – second mass loss

stretching carbon disulfide double bonds [9, 11]. Below the 1520 cm^{-1} region in the first mass loss spectra there are numerous peaks. Identification of these peaks is difficult and it is most probable that these peaks are due to vibrations associated with alkyl and carbonyl groups. Finally the peak at approximately 859 cm^{-1} has been attributed to stretching of the C-S double bond in carbonyl sulfide [8-10].

Conclusions

The py-GC-MS analysis of SEX was the only technique that permitted unambiguous identification of the evolved gases. The TG-MS mass spectra recorded were complex, consisting of molecular, fragment and isotope ion peaks of many gases. Thus identification of the molecular ions was reliant on the py-GC-MS data. Although SIM was used to monitor the molecular ions, the abundance was not accurate due to the possible overlapping of molecular and fragment or isotope ions. The infrared spectra of the mass losses were also complex. The spectra showed the presence of alkyl and carbonyl compounds, carbon disulfide, and carbonyl sulfide. Therefore this paper shows that TG-MS and TG-FTIR are insufficient for the identification and monitoring of gases in a complex mixture. Although py-GC-MS is suggested as an alternative identification technique, the high heating rate may affect both the relative abundance and the number of gases evolved.

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