

THE INFLUENCE OF ACTIVATED CARBON ON THE THERMAL DECOMPOSITION OF SODIUM ETHYL XANTHATE

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Abstract

The thermal decomposition of SEX in a nitrogen atmosphere was studied by coupled thermogravimetry-Fourier transform infrared spectroscopy (TG-FTIR), and by pyrolysis-gas chromatography-mass spectrometry (py-GC-MS). The TG curve exhibited two discrete mass losses of 45.8% and 17.8% respectively, at 200 and 257–364°C. The evolved gases identified as a result of the first mass loss were carbonyl sulfide (COS), ethanol (C₂H₅OH), ethanethiol (C₂H₅SH), carbon disulfide (CS₂), diethyl sulfide ((C₂H₅)₂S), diethyl carbonate ((C₂H₅O)₂CO), diethyl disulfide ((C₂H₅)₂S₂), and carbonothioic acid, O, S, diethyl ester ((C₂H₅S)(C₂H₅O)CO). The gases identified as a result of the second mass loss were carbonyl sulfide, ethanethiol, and carbon disulfide. Hydrogen sulfide was detected in both mass losses by py-GC-MS, but not detected by FTIR. The solid residue was sodium hydrogen sulfide (NaSH).

SEX was adsorbed onto activated carbon, and heated in nitrogen. Two discrete mass losses were still observed, but in the temperature ranges 100–186°C (7.8%) and 186–279°C (11.8%). Carbonyl sulfide and carbon disulfide were now the dominant gases evolved in each of the mass losses, and the other gaseous products were relatively minor. It was demonstrated that water adsorbed on the carbon hydrolysed the xanthate to cause the first mass loss, and any unhydrolysed material decomposed to give the second mass loss.

Keywords: activated carbon, adsorption, sodium ethyl xanthate, thermal decomposition

Introduction

Flotation reagents such as sodium ethyl xanthate (SEX) are widely used in the gold processing industry to separate gold bearing sulfidic ores from gangue material. The resulting concentrate is then oxidised or finely ground, and the gold recovered by leaching with cyanide solution. The resultant gold cyanide complex is adsorbed onto activated carbon which is separated from the pulp, and the gold recovered by leaching with an alkaline cyanide solution. Unfortunately the carbon is not very specific in its adsorption characteristics, and becomes considerably fouled by the adsorption of inorganic and organic species, which reduces its gold adsorption efficiency [1–3]. The fouled carbon is acid washed to remove inorganic mate-

rial, and thermally regenerated before being returned to the leach circuit. Thermal reactivation involves heating the fouled carbon to approximately 650°C for up to 30 min in steam but in the absence of air. During the regeneration process, any organic compounds present (such as SEX) are likely to be decomposed, with the production of gaseous effluent.

The decomposition of SEX is reported to produce gaseous COS and ethylene, with a solid residue of NaSH [4]. More recent studies have found dixanthogens, alcohols, elemental sulfur, dialkyl xanthates, thiols, and metallic sulfides [5], and CS₂, as well as aldehydes for the *n*-butyl and secondary butyl xanthates [6]. H₂S was also reported, although it was not detected in all experiments [6].

Very little work has been reported on the decomposition products of SEX adsorbed onto carbon [7]. Hence in this study, we report on the decomposition of SEX by itself, and adsorbed onto activated carbon. The work was carried out by coupled thermogravimetry-Fourier transform infrared spectroscopy (TG-FTIR). Pyrolysis-GC-MS was used to assist in the identification of gaseous products.

Experimental

SEX was obtained from Dow Chemicals and was recrystallised prior to use [5]. Based on a sodium analysis the percentage purity of the SEX was 95%. The FTIR spectrum agreed with that of pure SEX.

A peat based activated carbon, Norit 3515, was acid washed and conditioned before use [8]. The carbon was dried at 100°C and ground to <45 µm. SEX was loaded on the carbon by stirring 1 g samples at 400 rpm in 400 mL of 8.68×10⁻³ M SEX and a borax buffer (0.05 M, pH 9.18) at 20°C for 24 h. The carbon was separated using vacuum filtration, and stored in a desiccator for subsequent analysis.

Thermal analysis experiments were performed using a Netzsch STA-409 instrument fitted with a TG head interfaced via a transfer line heated to 200°C to a Bruker IFS 55 FTIR spectrometer fitted with a MCT (Hg-Cd-Te) detector. The Gram-Schmidt (GS) chromatogram, which measures the total gases evolved as a function of time, was recorded for all experiments.

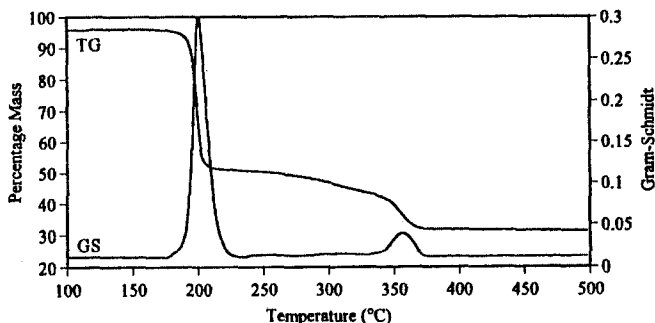


Fig. 1 TG-GS record of the thermal decomposition of SEX in nitrogen heated at 10°C min⁻¹

Pyrolysis Gas Chromatography/Mass Spectrometry (Py-GC/MS) experiments of a ground recrystallised sample of SEX, and a sample that had been previously heated to 210°C, were carried out with a Pyrojector microfurnace (SGE Scientific) interfaced via a capillary inlet system to a Hewlett Packard 5809A gas chromatograph fitted with a 50 m×0.25 mm i.d. WCOT fused-silica cross-linked methyl-silicone phase column (BP-1, film thickness 0.22 μm, Hewlett Packard). The SEX sample was diluted with ten times its weight of quartz. A pellet of this diluted sample was introduced directly into the pyrolyser which was maintained at 400°C. Helium was used as both pyrolysis and carrier gas (linear velocity 60 cm s⁻¹).

Results and discussion

Thermal analysis of SEX

The TG-GS record of the thermal decomposition of SEX heated at 10°C min⁻¹ in a nitrogen atmosphere is presented in Fig. 1. The TG curve showed two mass losses, a rapid mass loss of 45.8% commencing at 200°C, followed by a more gradual mass loss of 17.8% between 257–364°C. The GS curve showed two peaks which were coincident with the mass losses.

The FTIR spectra of the two mass losses are presented in Fig. 2. The spectrum of the gases evolved from the first mass loss at 200°C is complicated due to the number of overlapping peaks. Identification of these peaks was determined by comparing peak frequencies to characteristic infrared absorption frequencies of compounds identified as xanthate decomposition products [4–6]. Compounds that were

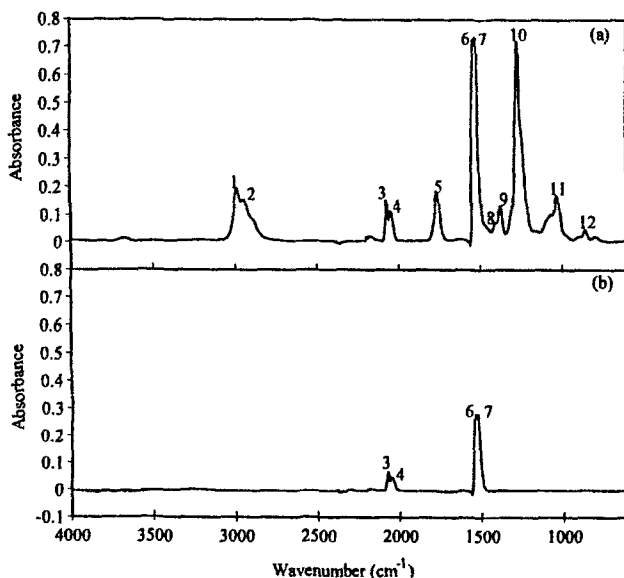


Fig. 2 Infrared spectra of the gases evolved from the two mass losses of the decomposition of SEX

identified as gases evolved in the first mass loss were alkyl compounds, carbonyl compounds, carbon disulfide, and carbonyl sulfide. However, these compounds did not account for all the observed peak frequencies. The identification of thiols, sulfides, and disulfides is only possible by identifying C–S stretching bands, which are very weak and occur below 650 cm^{-1} [9], which was outside of the range of the MCT detector ($4000\text{--}650\text{ cm}^{-1}$) used in this study. There was no evidence of alcohols present, as indicated by the absence of a broad band due to O–H stretching at $3600\text{--}3200\text{ cm}^{-1}$. Hydrogen sulfide absorbs weakly in the mid infrared region of the spectrum, and was not detected.

The infrared spectrum of the gases evolved from the second mass loss between $257\text{--}364^\circ\text{C}$ was less complicated than that of the first mass loss. The major gas evolved was CS_2 with a smaller amount of COS.

Pyrolysis GC/MS confirmed COS and CS_2 as decomposition products of the first mass loss. In addition, the alkyl compounds found in the FTIR record were identified as ethanethiol ($\text{C}_2\text{H}_5\text{SH}$), ethyl sulfide, and diethyl disulfide, as well as ethanol and possibly hydrogen sulfide [4, 6]. Two carbonyl compounds (which gave rise to the FTIR peak at 1759 cm^{-1}), diethyl carbonate and carbonothioic acid, O,

Table 1a Vibrational band assignments of the gases evolved from the first mass loss of SEX. Abbreviations: ν (stretch); ν_s , ν_{as} (symmetric, asymmetric stretch); δ (bending)

Peak	Wavenumber/ cm^{-1}	Assignment	Compounds	Refs
1	2983.5	$\nu_{as}(\text{CH}_3)$, $\nu_{as}(\text{CH}_2)$	ethene [$\nu_{as}(\text{CH}_2)$], ethanethiol	[10]
2	2948.0	$\nu_s(\text{CH}_3)$, $\nu_s(\text{CH}_2)$	diethyl sulfide ethyl carbonate diethyl disulfide carbonothioic acid, O,S-diethyl ester	
3	2071.5	$\nu_{as}(\text{C}=\text{O})$	carbonyl sulfide	[11–13]
4	2047.2	$\nu_s(\text{C}=\text{O})$		
5	1758.9	$\nu(\text{C}=\text{O})$	ethyl carbonate carbonothioic acid, O,S-diethyl ester	[14]
6	1531.3	$\nu_{as}(\text{C}=\text{S})$	carbon disulfide	[9, 12]
7	1524.2	$\nu_s(\text{C}=\text{S})$		
8	1404.8	$\delta(\text{C-H})$ of CH_2 , CH_3	same as peaks 1 and 2	[14]
9	1376.2	$\delta(\text{C-H})$ of CH_3 ,	same as peaks 1 and 2	[14]
10	1265.7	$\nu(\text{C-O})$	ethyl carbonate carbonothioic acid, O,S-diethyl ester	[14]
11	1026.1	$\nu(\text{C-O})$	ethyl carbonate carbonothioic acid, O,S-diethyl ester	[14]
12	859.4	$\nu(\text{C}=\text{S})$	carbonyl sulfide	[11–13]

Table 1b Vibrational band assignments of the gases evolved from the second mass loss of SEX. Abbreviations: ν_s , ν_{as} (symmetric, asymmetric stretch)

Peak	Wavenumber/cm ⁻¹	Assignment	Compounds	Refs
3	2071.5	$\nu_{as}(\text{C}=\text{O})$	carbonyl sulfide	[11–13]
4	2047.2	$\nu_s(\text{C}=\text{O})$		
6	1540.2	$\nu_{as}(\text{C}=\text{S})$	carbonyl disulfide	[9, 13]
7	1524.4	$\nu_s(\text{C}=\text{S})$		

S-diethyl ester, were found which have not been previously reported. COS and CS₂ were confirmed as the second mass loss decomposition products along with hydrogen sulfide.

From the pyrolysis GC/MS analysis, all the peaks of the gases evolved from the first and second mass losses could be positively identified. The identity of each peak in the infrared spectra of the first and second mass losses is presented in Tables 1(a) and 1(b).

Thermal analysis of SEX adsorbed on activated carbon

The thermal decomposition of SEX adsorbed on activated carbon was investigated using Norit 3515 activated carbon of particle size <45 μm , with a SEX loading of 32.5%. The TG-GS records of a sample of the unloaded carbon, together with a sample of the carbon loaded with 32.5% SEX, heated in a nitrogen atmosphere at 10°C min⁻¹, are presented in Fig. 3.

With the unloaded carbon, a total mass loss of 6.2% was observed, which occurred in two distinct mass losses, the first at 150–400°C and a larger mass loss at 650–1000°C. Both these mass losses are attributed to the decomposition of the carbon to carbon dioxide and carbon monoxide, which were detected by FTIR. The concentration of carbon dioxide was greater than carbon monoxide.

The TG and GS curves of the SEX/Norit 3515 coincided, and showed two significant mass losses of 7.8 and 11.8% respectively in the temperature ranges 100–186 and 186–279°C. The infrared spectra of the gases evolved during the two mass

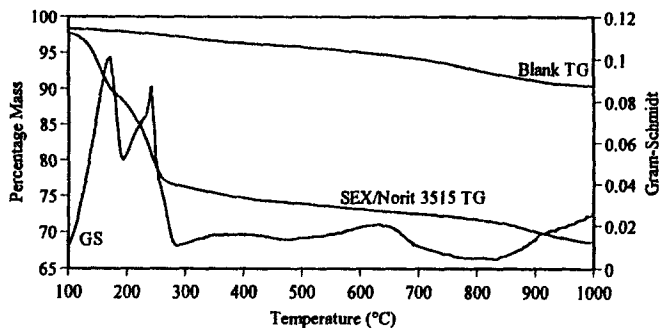


Fig. 3 TG-GS records of the thermal decomposition of SEX adsorbed on Norit 3515 and the corresponding blank TG curve. Nitrogen atmosphere, heating rate 10°C min⁻¹

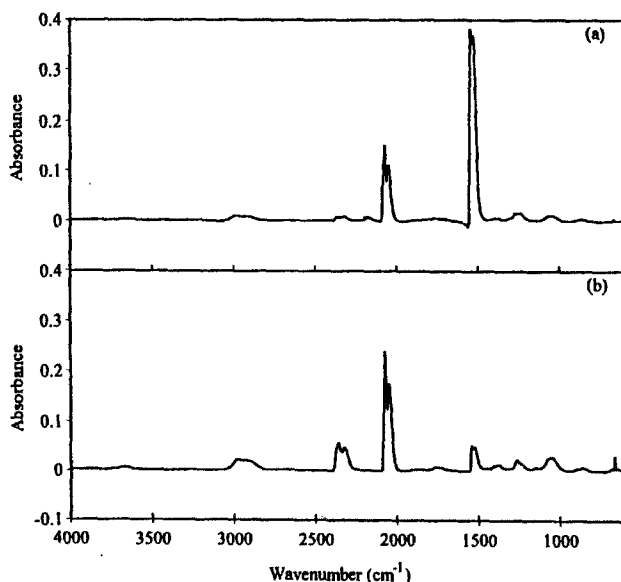


Fig. 4 Infrared spectra of the gases evolved from the two mass losses during the decomposition of SEX adsorbed on Norit 3515

losses are presented in Fig. 4. The gases evolved from both mass losses were mainly carbonyl sulfide and carbon disulfide. Other minor bands present were indicative of smaller abundances of other organic compounds resulting from the decomposition of SEX.

Comparison of thermal decomposition of SEX alone and adsorbed on activated carbon

It is evident from an inspection of the TG-GS curves (Figs 1 and 3) and the FTIR spectra of the evolved gases (Figs 2 and 4) that SEX decomposes differently when adsorbed on activated carbon. When adsorbed on activated carbon, the first mass loss results in the evolution of CS₂ and COS. The second mass loss is similar to the first mass loss of SEX by itself, except that the abundance of CS₂ has decreased and that of COS has increased. There is no mass loss equivalent to the second stage decomposition of SEX by itself, that is in the temperature range 257–364°C.

One of the reactions that produces carbon disulfide is hydrolysis of the SEX, which under neutral to mildly alkaline conditions occurs via the following equation [5, 15].



Although the reaction is relatively slow at ambient temperatures, at elevated temperatures the rate of reaction is increased considerably [5]. Activated carbon ad-

sorbs water from aqueous solution. To demonstrate the temperature regions where water evaporates, Norit 3515 was immersed in water for 24 h and air dried. The TG curve indicated that most of the water was evolved from the system between 20–130°C, with the most rapid mass loss taking place at 100°C as the water boiled off. Water continued to be evolved, together with CO and CO₂, although at a lesser rate, above 130°C. Hence during the loading of SEX onto the carbon both water and SEX will be adsorbed. As the sample is heated water can react with the SEX according to the equation given above.

Experiments were performed to test the hydrolysis theory by heating SEX in the presence of varying amounts of deionised water. Mass ratios used were 16:1 (stoichiometric ratio), 1:1, and 1:16 of SEX-water. Figure 5 shows the TG curves

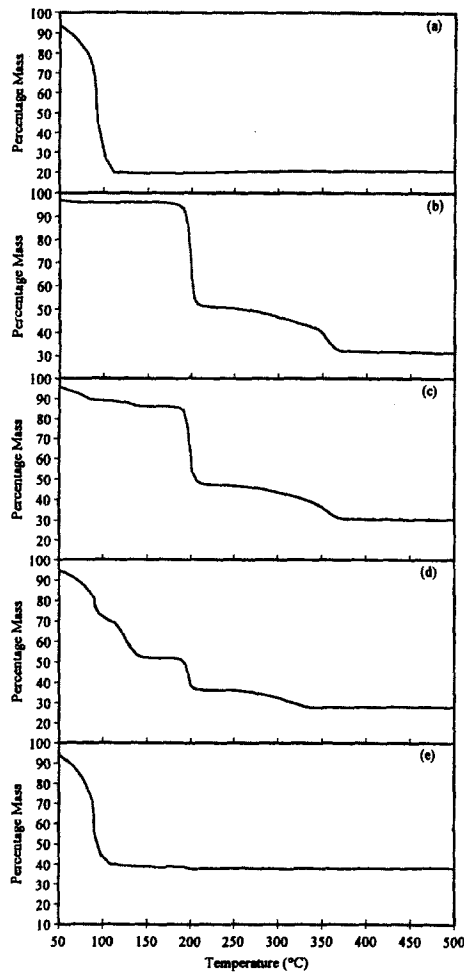


Fig. 5 TG curves of: a) deionised water; b) SEX; c) mixture of 16:1 SEX:water; d) mixture of 1:1 SEX:water; and e) mixture of 1:16 SEX:water. Heating rate 10°C min⁻¹, in nitrogen

of these mixtures, water by itself and SEX by itself. The experiments were performed using platinum crucibles and lid with a pinhole, which provided a self-generated atmosphere of water vapour to react with the SEX.

All the TG curves of the SEX-water ratios, except 1:16 ratio, have four mass losses. A comparison of the SEX-water TG curves to the water TG curve indicates the first mass loss is due to water. A comparison to the TG curve of the SEX indicates the third and fourth mass losses are due to the two thermal decomposition reactions of SEX. These observations are also supported by the spectra of the mass

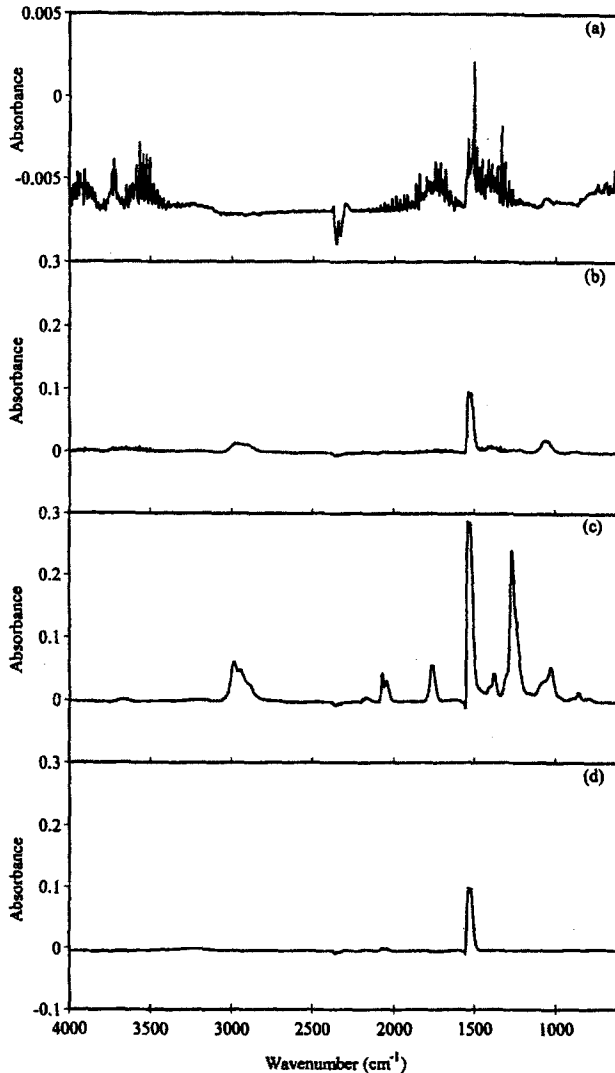


Fig. 6 FTIR spectra of the four mass losses observed in the TG curves for the 1:1 ratio of SEX:water as shown in Fig. 5(d). a) first mass loss b) second mass loss c) third mass loss d) fourth mass loss

losses, which are shown in Fig. 6. However, the second mass loss product(s) could only be determined by observing the FTIR spectrum (Fig. 6b), which shows carbon disulfide is formed, which was attributed to the hydrolysis of the SEX. From these experiments it is evident that the presence of water will cause carbon disulfide to evolve before the thermal decomposition of the SEX.

Table 2 Mass losses of the TG curves in Fig. 6

TG curve	Mass loss/ %			
	50–104°C	104–136°C	200°C	250–368°C
SEX	No mass loss	No mass loss	45.8	17.8
16:1 SEX-H ₂ O	4.3	2.6	37.9	17.2
1:1 SEX-H ₂ O	23.0	18.0	16.0	7.8
1:16 SEX-H ₂ O	55.1	0.9	1.4	Not detected

Table 2 shows the temperature ranges at which mass losses occurred for the various TG curves of Fig. 5. It is apparent that as the ratio of water to SEX increases, SEX is increasingly hydrolysed and the total mass loss above 200°C decreases from 65.1% to 1.4%. This data supports the suggestion that when SEX is adsorbed onto activated carbon, and that the first reaction to be observed is the hydrolysis of SEX, followed by thermal decomposition of any unreacted SEX.

Conclusions

The thermal decomposition of SEX occurred in two distinct stages. The first stage produced a complex mixture of gases, whilst the second stage produced mainly carbonyl sulfide, carbon disulfide and H₂S. Adsorption onto activated carbon altered the reactions sequence. It was demonstrated that water adsorbed on the carbon caused partial hydrolysis of the SEX in the region of 100–186°C, and carbonyl sulfide and carbonyl sulfide were the major gases produced. Remaining unreacted SEX then underwent further reaction between 186–279°C, to give an evolved gas profile that was similar to that obtained in the first stage decomposition of SEX by itself. However, COS was now the dominant gas, and the other gases had diminished relatively in importance.

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Mr. N. G. Fisher would like to thank the A. J. Parker CRC for Hydrometallurgy for the provision of a PhD scholarship.

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