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Infrared spectroscopic determination of the gas-phase thermal decomposition products of metal-ethyldithiocarbonate complexes

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Abstract

Head-space analysis by gas-phase infrared spectroscopy (HAGIS) allows the facile examination of the decomposition mechanisms of the metal xanthates [metal-(O-alkyldithiocarbonates], Fe(EtOCS₂)₃, Zn(EtOCS₂)₂, Cu(EtOCS₂)₂, Pb(EtOCS₂)₂ and Ni(EtOCS₂)₂, over the temperature range 25–120°C. These metal xanthates fall into two groups based on the generation of the primary gaseous decomposition products, CS₂, COS and CO₂. The first group, consisting of Fe(III) and Zn(II) xanthates, decompose readily, forming mostly CS₂ and COS in a constant ratio and leaving, initially, a metal-alkoxide residue. In the second group, decomposition is relatively small, generating CO₂ and COS, with the proportion of COS increasing as the temperature increases and CS₂ formation occurring only at the upper end of the temperature range. The residue is more of a metal-thioalkyl species in this case. Presumably, CO₂ is formed by re-insertion of COS into a metal alkoxide and elimination of CO₂, leaving a thioalkyl moiety. Volatile metal-xanthates are probably observed in the gas-phase, allowing examination of the changes concomitant to the vaporization of the discrete metal xanthates from network or partially associated solids. © 1997 Elsevier Science B.V.

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1. Introduction

Metal-xanthates [metal-(O-alkyldithiocarbonates), M-(S₂COR)_n] are of considerable interest from several viewpoints. As simple, relatively stable examples of metal polysulfide coordination, they can serve as models for more complex systems and help to elucidate the principles which govern the chemistry of such materials. Moreover, these ligands can form bidentate chelates, or monodentate discrete or network solids, showing a wide range of coordination behaviour [1]. The ligands themselves can be varied by modification of the alkyl chain to access a host of electronic and steric environments, as well as inducing changes in solubility and other physical attributes.

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Spectroscopically, these complexes are of interest because of the complex interplay of the C-S and C-O vibrational modes [2]. These modes and those of the M-S fragments are strong in both the infrared and Raman spectra due to strong dipole moments and the highly polarizable sulfur atoms, respectively. Finally, and most importantly, since metal ions are freed from mineral surfaces during commercial flotation processes, which often involve the use of xanthate collectors, metal xanthates may play a role, or at least are present, in mineral extraction [3].

Thermal decomposition of metal xanthates holds some relevance to many of these aspects of their chemistry. For instance, synthetically, this approach affords a relatively low-temperature route to metal oxides and sulfides and, in particular, nickel ferrites, which are formed from mixed nickel/iron xanthates [4]. From a mineral processing standpoint, possible decomposition of metal xanthates on surfaces can significantly alter the surface properties crucial to the separation process. Gaseous decomposition products from stored metal xanthate coated materials after separation may also pose an environmental problem [3].

The importance of these questions has not been ignored, with a number of studies of the decomposition of metal-xanthates being reported over the years. Activation energies have been determined from TG, DTG and TGA [4-6] measurements and the residues have been characterized as mostly metal sulfides at low temperatures and metal oxides at higher temperatures. The volatile decomposition products have been analyzed by mass spectrometry and identified as chiefly COS and CS_2 [6], all of which pose safety hazards. Although a considerable amount is known about the above processes, the conditions and mechanisms for formation of the various products are still unclear. We have recently begun a broad investigation of the volatile products from thermal decomposition reactions by head-space gas phase FT-IR spectroscopy (HAGIS) [7]. In this paper, we report the results of an examination of the thermal decomposition of selected metal xanthates by the HAGIS technique.

2. Experimental

Potassium ethyl xanthate, $[K(S_2COC_2H_5)]$, was purchased from Cyanamid. The metal salts, ¹³Clabeled CS₂ (99 + atom %) and 2.2,2-d₃-ethanol (99 + atom %) were supplied by Aldrich. Labeled potassium xanthate was synthesized and purified according to standard literature methods [8]. The metal xanthates, $Fe(EtOCS_2)_3$, $Ni(EtOCS_2)_2$, $Zn(EtOCS_2)_2$ and $Pb(EtOCS_2)_2$, were synthesized by modified literature methods [9]. Generally, 5 g of the appropriate water soluble metal salt $[Fe_2(SO_4)_3, NiBr_2, Pb(NO_3)_2 \text{ or } ZnSO_4]$ was dissolved completely in 20 ml cold water and then treated with a slight excess of freshly recrystallized (acetone/petroleum ether) potassium ethyl xanthate in 5 ml water. The solids which were formed instantly were filtered off and washed thoroughly with cold water. The compounds were recrystallized from appropriate solvents [9] and were stored in the freezer prior to use. Copper(I) ethyl xanthate was prepared directly according to the literature procedure [9] and was used immediately in the unrecrystallized form. The labeled metal complexes were synthesized in a similar manner from the appropriate metal salt and labeled potassium ethyl xanthate.

The head-space gas-phase FT-IR spectroscopic technique (HAGIS) has been described in detail elsewhere [7]. Briefly, a small sample of the solid metal xanthate is heated on a metal sample stage well removed from the spectrometer beam. The FT-IR spectrum of the gaseous species above the sample is recorded after a 5 min equilibration period has elapsed. In the present work, all the samples were heated in vacuo at about 0.05 torr. The IR spectra were recorded at a nominal resolution of 4 cm⁻¹ on either a Bruker IFS-88 or IFS-66 FT-IR spectrometer, both of which were equipped with a liquid N₂-cooled MCT detector.

The metal-xanthates, $Fe(EtOCS_2)_3$, $Zn(E-tOCS_2)_2$, $Cu(EtOCS_2)$, $Pb(EtOCS_2)_2$ and $Ni(-EtOCS_2)_2$, were each examined over the range 25–120°C. In addition, the representative complexes, $Zn(EtOCS_2)_2$ and $Pb(EtOCS_2)_2$, were studied over additional time intervals of 5, 15, 30, 45 and 60 min, in order to define the kinetic constraints of the system. As background references,

potassium ethyl xanthate and diethyl dixanthogen were also examined.

3. Results and discussion

The metal xanthates selected for this study span a variety of properties of the metal, the xanthate and the solid as a whole. Electronically, the metals range from Fe(III) (d⁶), through Ni(II) (d^8) , Cu(I) (d^{10}) and Zn(II) (d^{10}) to Pb(II) $(d^{10}s^2)$. Stereochemically, Fe(III) forms a discrete octahedral complex [1](a), (b), Ni(II) a discrete regular square-planar complex [1](d) and Pb(II) a distorted tetrahedral complex with two short and two long bonds [1](e). Zinc(II), on the other hand, forms a network solid containing repeating Zn₄ squares, with tetrahedral coordination around the zinc atoms [1](c). The structure of the Cu(I) complex is unknown. In terms of the xanthate ligand, it is clearly bidentate chelating [1](a), (b) and (d) around iron and nickel, with equal metal-S and C-S bonds. In the lead(II) complex, the xanthate is unsymmetrical with one long and one short metal-S bond in each xanthate moiety but with equal C-S distances, indicating still considerable charge delocalization over the CS_2 units [1](e). For the Zn(II) complex, the xanthate is once again symmetric, bridging two separate zinc atoms [1](c), with each zinc atom being bound to four different xanthate ligands.

All of the complexes examined showed measurable gaseous products at between 30 and 40°C. Examples of the FT-IR spectra obtained for one of the compounds in the temperature range 25-120°C are presented in Fig. 1. In all cases the spectra have been ratioed against the loaded cell at room temperature so that the observed products are all the result of thermal processes. After 5 min equilibration, the temperature was stable and this was selected as the measurement time, primarily for comparison with the use of this technique in the rapid analysis of mineral samples [7]. The results obtained at this time were readily reproducible. Moreover, the variations with time (vide infra) are small compared with the variations over the $\sim 20^{\circ}$ C temperature increments used in the present study, or with variation of the metal. Hence, the products formed at the 5 min time interval should be comparable, within an error of a few percent.

3.1. Triatomic gaseous products

Four simple gaseous products, CO₂, COS, CS₂, and CO, were observed in the thermal decomposition of the metal xanthates, in agreement with earlier mass spectrometric determinations [6](a). The band intensity distributions for the compounds at all the measured temperatures are presented in Table 1. At higher temperatures, one or more complex species, containing bands in the C-H stretching and fingerprint regions are produced. All of these decomposition processes appear to occur at considerably lower temperatures than do those reported by TG, TGA and DTA methods [4-6]. By contrast, neither potassium ethyl xanthate nor diethyl dixanthogen, the primary oxidation product of xanthate on metal and mineral surfaces, afforded appreciable amounts of these gaseous products under the same conditions used for the metal complexes. Therefore, the products described are unique to the complexed xanthate species.

There are two very distinct groupings of the xanthate complexes, based upon the simple gaseous species generated during heating. The first group, consisting of Fe(III) and Zn(II) xanthates,



Fig. 1. Typical HAGIS spectra of (a) $Pb(EtOCS_2)_2$ and (b) $Fe(EtOCS_2)_3$ over the range $80-120^{\circ}C$.

Table 1

Distribution of simple di- and tri-atomic gas-phase species and total integrated intensity of the associated IR bands above $Fe(EtOCS_2)_3$, $Zn(EtOCS_2)_2$, $Cu(EtOCS_2)_2$, $Pb(EtOCS_2)_2$ and $Ni(EtOCS_2)_2$ over the temperature range 25-120°C

Complex	Temperature (°C)	CS ₂ ^a	COS ^b	CO ^b ₂	CO ^b	Total
First Group				······································		
Fe(EtOCS ₂) ₃	37	59	40	0	0	0.1
	60	57	36	6	0	1.7
	80	59	36	3	2	9.7
	100	58	36	3	2	33.6
	120	56	38	3	2	58.6
Zn(EtOCS ₂) ₂	43	56	19	23	2	0.3
	60	50	30	19	1	1.0
	80	51	39	9	1	3.7
	100	51	38	9	1	11.6
	120	48	40	10	2	15.1
Second Group						
$Pb(EtOCS_2)_2$	40	0	17	83	0	0.1
	60	0	38	62	0	0.2
	80	0	49	51	0	0.4
	110	17	46	26	0.5	2.3
Ni(EtOCS ₂) ₂	35	0	0	100	0	0.1
	53	0	0	100	0	0.2
	70	13	0	87	0	0.3
	85	16	2	82	0	0.4
	100	18	4	77	0	0.5
	120	20	10	70	0	0.6
Cu(EtOCS ₂)	43	0	21	79	0	0.1
	80	19	39	42	0	0.7
	100	15	65	20	0	1.6
	120	11	78	11	0	3.4

Integrated intensity as a percentage of total ^a Antisymmetric C–S stretching mode (1535 cm⁻¹) and ^b C–O stretching modes (CO₂, 2349; COS, 2062; and CO, 2180 cm⁻¹).

^c Total integrated intensity of all bands.

shows substantial quantities of a few gaseous products, even at low temperatures, and each is present in at least twice the amount seen for any member of the other group. This situation is shown for the example of COS in Fig. 2. Moreover, the relative proportions of the products are constant, independent of the temperature, within the significance of the experimental technique. Within this group, Fe(III) xanthate is consistently higher in gaseous product output than is Zn(II) xanthate by a factor of up to three (at 120°C). The constant ratio of the proportions is similar, if not identical, for the two metal moieties at around 55% CS₂:35% COS:5% CO₂:5% CO.

It should be noted that these percentages are based on intensity ratios only. No reliable means of calculating the partial pressures of the gas phase species was devised. The primary difficulty in relating the IR absorbance intensity and partial pressures for each component arises from line broadening due to temperature and pressure effects. Furthermore, the temperature of the gas phase species was not known (only the temperature of the solid could be measured). As a result of these factors, any attempt to determine the partial pressure of the substituents of the mixture would involve assumptions and estimates that would render the result invalid and potentially misleading.

In the second group, consisting of Ni(II), Cu(I) and Pb(II) xanthates, the products differ considerably from those of the first group. The amounts of the products formed are significantly reduced at all temperatures. At temperatures below 80°C, CS_2 , the most prominent product for the first group, is not observable in detectable amounts. Carbon monoxide is not present in the spectra of this group except at over 110°C in the case of Pb(II) xanthate. For this single example, this corresponds to a significant increase in the concentration of CS_2 at this temperature. Also, the product ratio in this second group is not constant, unlike that observed for the other group. At just above room temperature, CO_2 is dominant in the spectrum, with lesser amounts of COS being formed. Small amounts of CO_2 may be produced from gas trapped in the cell, particularly on the surface of the metal sample boat. For Zn(II), the CO₂ level is constant at an integrated absorbance of 0.2 for 1 h at 60°C, yet increases with time, similarly to the other species, at higher temperatures. This implies that, at lower temperatures, most, if not all, of the CO₂ arises from desorption and that, only at higher temperatures, does the generation of CO_2 from xanthate decomposition become significant.



Fig. 2. Generation of COS by $Fe(EtOCS_2)_3$ (\blacksquare), $Zn(EtOCS_2)_2$ (\bullet), $Cu(EtOCS_2)$ (ϕ), $Pb(EtOCS_2)_2$ (\checkmark) and $Ni(EtOCS_2)_2$ (\blacktriangle) on heating between 25 and 120°C.



Fig. 3. HAGIS spectra of the head-space above (a) Fe(E-tOCS₂)₃ and (b) Fe(EtO¹³CS₂)₃ in the region of CO₂, CO, COS and CS₂, demonstrating that the majority of the simple di- and tri-atomic species generated arise from the C₁ carbon center.

The spectrum of the gas-phase products above an isotopomer of Fe(EtOCS₂)₃, at 120°C, labeled at the C₁ position of the xanthate ligand with C-13, synthesized from $[^{13}C_1]$ ethyl-xanthate, is shown in Fig. 3. It can be seen that both labeled and unlabeled CO₂ are present in similar amounts. Hence, about 50% of the observed CO₂ results from decomposition of the metal xanthate for this species, at this temperature. At 60°C, only unlabeled CO₂ is observed, at an integrated absorbance of 0.18, similar to that observed for Zn(II) xanthate at this temperature. Presumably, the rate of desorption of CO_2 from the boat is relatively constant, regardless of the metal complex examined. Therefore, for complexes which do not produce such large amounts of gaseous products, the ratio of CO_2 from xanthate decomposition to CO_2 desorbed from the cell is considerably less. Fig. 4 shows the variation in product distributions with temperature for Pb(II) xanthate. The relative band intensity of COS increases with temperature until it becomes the dominant feature, except in the case of Ni(II) xanthate, where, while



Fig. 4. Distribution of the simple gaseous products, COS (\bullet), CO₂ (\blacksquare), CS₂ (\blacktriangle) and CO (\blacktriangledown) from decomposition of Pb(EtOCS₂)₂ over the temperature range 25-120°C.

this trend is also observed, COS does not become dominant in the available temperature range (Fig. 5). The absolute output is considerably lower for Ni(II) xanthate than for any other metal xanthate at all temperatures. Above 80°C, CS_2 is generated



Fig. 5. Distribution of the simple gaseous products, COS (\bullet), CO₂ (\blacksquare), CS₂ (\blacktriangle) and CO (\checkmark) from decomposition of Ni(EtOCS₂)₂ over the temperature range 25-120°C.

in increasing amounts for the Cu(I) and Pb(II) xanthates. In particular, for Pb(II) xanthate, the production jumps from an undetectable amount at 80°C to over 25% of the overall band intensity of the simple gaseous products formed at 110° C. Small amounts of CO also appear at this temperature.

In the C₁ labeling experiment described earlier, all of the simple products appear to arise mainly from decomposition of the alkyl xanthate moiety (i.e. all are mostly ¹³C-1 labeled, except for CO₂, as described above). Small amounts of unlabelled products probably result from the presence of unlabelled CO₂, which can cause scrambling of the label by re-insertion into the metal complex, as will be described later.

For both groups of xanthate complexes, there are no signs of simple (up to C_5) alkanes, alkenes or alkynes in the head space, although some alkyl-containing materials are apparently present at higher temperatures. Such simple alkane products could reasonably be expected in the decomposition of alkyl xanthates and have been observed previously in thermal decomposition experiments [6](b). Other possible alkyl-containing species such as thiols, ethers and thioethers also appear to be absent, implying that, for the most part, the alkyl groups remain tied to the involatile metallic residues in the sample boat. One simple alkyl component of the gas phase which has been identified is ethanol. The production of this component is greatest in the first group of metal xanthates and is completely absent in the cases of Ni(II) and Cu(I) xanthates.

It is clear from our results that the first group of metal xanthates follows a very well defined thermal decomposition pathway, leading to a constant ratio of products, regardless of temperature. The implications of this conclusion are that either of two conditions apply. Firstly, all the products may be produced in a single process such that each product is associated with the others. It is difficult to envisage such a concerted process. If there were several different processes combining to form these gases, they would all have to have the same, or at least very similar activation energy in order that the product distribution be constant. For the minor products, CO and CO_2 , it is possible that there is some variation in the proportions but this is small in relation to the major products and does not appear significant. From both groups, it seems that CO production is linked to the generation of CS_2 and of CO_2 .

In the second group of metal xanthates, several different reactions occur at all stages of the decomposition process. The production of CO_2 and COS, the major processes observed at low temperatures, are independent of each other. This observation implies that separate mechanisms are responsible for the formation of each species. However, the extent of decomposition at these temperatures is very small compared with that of the other group. At around 80°C, CS₂ production begins (except in the case of $Ni(EtOCS_2)_2$) and the rate of CO₂ and COS production also increases dramatically. Small amounts of CO are observed following CS_2 production. The implication is that the mechanism responsible for the rapid decomposition of the first group of materials is competitive with other processes in the low-temperature range. Unfortunately, since higher temperatures were unavailable to our technique, it is difficult to ascertain whether, at higher temperatures, this becomes the dominant process, as for the first group of metal xanthates.

The two groupings of metal xanthates do not correspond directly to any of the properties of the metals themselves. Structurally, the Fe(III) and Zn(II) xanthates are at opposite ends of the scale, with iron(III) forming a discrete chelated xanthate complex and zinc(II) forming a network solid containing metal-metal bridging xanthates. Electronically, they could be considered to have similar properties on the basis of their filled (Zn(II))or half-filled (Fe(III)) configurations. However, Cu(I) and Pb(II) also fit this description and the Cu(I), Pb(II) and Zn(II) ethyl xanthates have been classified together and separate from nickel(II) and iron(III) on the basis of infrared data [2](d). Also, Fe(III) xanthate apparently forms a mostly low-spin complex [1](b) although this can be thermally modified in similar systems [10]. Likewise, there are no similarities in structure or electronic configuration which link the Ni(II), Cu(I) and Pb(II) xanthates.

One way to view this decomposition process is to examine the product distribution in terms of the dithiocarbonyl moiety alone. This proposal can be justified on the basis that the alkyl-containing functionality does not appear in this series of products and is constant for all the substrates. This implies that, for the process which results in the formation of the triatomic gases, the alkyl groups remain attached to the metal center. Hence, some form of migration of the ethyl groups, either directly to the metal, or to an oxo or sulfido functionality on the metal is required. The gaseous products must, then, arise from the dithiocarbonyl moiety alone, as was confirmed by the ${}^{13}C_1$ -labeling experiment. This dithiocarbonyl group has a nominal composition of COS₂. For the first group of metal xanthates, where the product distribution is constant at all temperatures, the products are mostly CS_2 and COS. This ratio is clearly depleted in oxygen from the original composition, even allowing for the small amounts of CO₂ and CO formed and may be slightly depleted in sulfur. If the relative molar absorptivities are assumed to be equal, the final distribution contains 50% of the initial oxygen and 75% of the original sulfur, relative to carbon. Most likely, a lower molar absorptivity for CS, than COS applies and the system is even more oxygen depleted. By contrast, the distribution of triatomic gases for the second group of metal xanthates is variable but, even at 120°, where CS₂ production has started, it is strongly depleted in sulfur but contains most of the oxygen (relative to carbon) found in the original dithiocarbonates. At lower temperatures, below where appreciable CS_2 production has started, the gas phase is very rich in oxygen and exceedingly low in sulfur. In the case of $Ni(EtOCS_2)_2$, this situation applies over the whole temperature range studied.

Based on these observations, the driving force for the reaction in the first group of metal xanthates may be the type of residue formed. The affinity of iron(III), a small, hard cation, for alkoxy ligands rather than thiolates may drive the reaction to produce this type of residue. Transfer of an ethoxy group from xanthate to the metal would leave a CS_2 species as the major product of this reaction (Scheme 1). Migration of the alkyl



Scheme 1. Origin of triatomic gas-phase species. (i) Metal-S bond breaking; (ii) S-C bond rotation; (iii) alkyl migration from O to S; (iv) Elimination of triatomic species to form a metal alkoxide or thioalkyl species.

group from oxygen to sulfur, producing an O,Sbound S-ethyl dithiocarbonate isomer, followed by a process similar to that for CS_2 leads to COS(Scheme 1), the other major product. However, for iron(III) and zinc(II) xanthates, the predominant decomposition reaction produces a constant ratio of CS₂ to COS and other minor products. This result implies that there is a single process which produces both CS₂ and COS. Because of the difficulties involved in obtaining relative molar absorptivity data, it is not possible to determine whether the actual ratio of these products is 1:1. However, it seems unlikely that any other ratio could result from a single process. Alternatively, in order to obtain a constant ratio of products at all temperatures, the two processes which produce the different products must have closely similar activation energies.

Two explanations are possible: First, the ratedetermining step may be the cleavage of a metal-S bond, allowing, in some cases, transfer of the alkyl group to the sulfur (a low energy process) or rotation to bring the alkoxy group closer to the metal, facilitating transfer of the alkoxy group to the metal. This explanation appears to be the simplest but it would seem unusual that Pb(II) xanthate should lie in the variable group as lead(II) xanthate already has one stretched metal-S bond in each xanthate ligand, although this compound approaches the borderline between the two groups. Alternatively, but less likely, initial formation of the metal alkoxide greatly accelerates the rate of the second reaction. In either scenario, the connection with the production of CO is unclear.

The greater affinity of the larger metal centers, Ni(II), Cu(I) and Pb(II), for sulfur ligands makes the above metal-S cleavage a higher energy process for the xanthate complexes of these metals compared with those of the other group of metal xanthates. Hence, the ground state is of lower energy and only more complex processes, which produce highly oxygenated species, such as CO₂ and COS, are found to occur for the second group. For this reason, the absolute decomposition rate is very low in comparison with the first group metal xanthates. In order to form CO₂, another oxygen atom must be made available. Since these experiments were performed in vacuo, specifically to eliminate oxidation reactions, the additional oxygen atom must arise from other xanthate ligands. As the reaction is reversible, it could be formed from the insertion of COS, formed in the initial elimination, into a metalalkoxy bond to form a monothiocarbonate, which, by a similar process, could rearrange and eliminate CO_2 , leaving a thioalkyl group on the metal (Scheme 2). That the CO_2 arises from the C_1 carbon of a xanthate ligand is confirmed by the ¹³C-labeling experiments. The COS formed from these compounds is presumably from the series of steps described for the first group metal



Scheme 2. Origin of CO_2 . (i) Insertion of COS into a metal alkoxide to form a metal monothiocarbonate; (ii) alkyl migration from O to S followed by elimination of CO_2 , leaving a metal-thioalkyl species.

xanthates. The low affinity of the metals in this group for alkoxy species, however, makes the CS_2 forming process slow and rapidly reversible, hence the higher CO_2 content. Since the formation of CO_2 requires some CS_2 production, this is presumably also present but the lower molar absorptivity of the CS_2 vibration makes it relatively more difficult to measure at the low concentration levels present.

In summary, COS and CS_2 are probably formed in a two-step process, where metal–S bond cleavage is followed by rotation and metal– O bond formation. A competitive alkyl migration from oxygen to sulfur followed by rotation and metal–S bond formation results in COS. Where these reactions are slow, the reverse reaction becomes more favorable (i.e. the equilibrium lies towards the complex) and CO_2 can be formed. For iron(III) and zinc(II) xanthates, the former equilibria lie strongly in favour of the gaseous products and so COS and CS_2 are the major products. For nickel(II), lead(II) and copper(I) xanthate, the equilibria lie towards the solids and more sulfurated metal species may result.

3.2. Alkyl products

Earlier, we mentioned the presence of other IR bands in the C-H stretching region and in the fingerprint region. The variation of the relative intensities of these bands indicates that there are two species present. The first species, which is constant for all metals and is not sensitive to C_1 labeling, can be identified easily as ethanol from the bands at 1394, 1242 (partially obscured by bands from the later product) and 1066 cm⁻¹, all of which show rotational fine structure and are sensitive to deuteration of the terminal methyl group of the xanthate, moving to 1385, 1160 and 1040 cm⁻¹, respectively. The O-H and C-H bands at 3676 (labeled band obscured by the C-H bands of undeuterated carbons) and 2972 (2256 labeled) cm^{-1} , respectively, and a weaker band at 868 cm⁻¹ confirm this assignment. Ethanol is clearly formed from the metal-alkoxide residue left after CS₂ elimination. This suggestion is confirmed by the correlation between ethanol generation and metal xanthates which produce



Fig. 6. HAGIS spectra of (a) $Fe(EtOCS_2)_3$ and (b) $Fe(EtO^{13}CS_2)_3$ in the region of C-O and C-S stretching vibrations, marking the shift of bands on ${}^{13}C_1$ -labeling. Bands labeled * are due to ethanol. This species does not contain any of the C₁ carbon.

 CS_2 . Variation within this grouping presumably arises from the relative abilities of the metals to abstract a hydrogen atom from other alkyl groups to form the alcohol. Interestingly, there is no corresponding production of ethanethiol in either group of metal xanthates, in particular the second group, where a metal-thioalkyl residue is expected. The implication is that either the thioalkyl is unable to abstract hydrogen from other ligands or that the metal-thioalkyl is considerably more stable than is the ethoxy complex.

When the ethanol bands are eliminated, there are still some features remaining, which shift to lower energies by a factor of between 1.02 and 1.04 on ${}^{13}C_1$ -labeling (Fig. 6), consistent with C-C, C-O or C-S stretching bands, and vary dramatically with the metal center involved (Fig. 7). The intensities of these bands vary, relative to the ethanol bands and those of the CO species but are self-consistent. These bands do not correspond to any alkyl species which could reasonably be expected to be formed from the metal xanthates such as Et₂S, Et₂S₂ [11] or EtOC(S)SEt [12].

of which the latter has been detected by mass spectrometry [6]. In fact, the bands appear to be similar in pattern to those of a coordinated metalxanthate species. Several of the complexes visibly sublime from the sample boat onto the walls of the cell at elevated temperatures, so it is possible that the observed bands arise from the metal complex in the gas phase. Gas-phase IR spectra of these complexes have not been reported previously. In the fingerprint region, the bands at ca. 1200 cm⁻¹ due to mostly C_1 -O and C_2 -O stretching [2], those at 1150 and 1040 cm⁻¹ due to C-S mixed with C-O stretching and those at 870 cm⁻¹ due to C_2 -C stretching are prominent and even occur at approximately the same relative intensities as in the parent metal xanthates. The bands are, however, shifted significantly from those observed for the solid metal xanthates (Table 2). The C_1 -O stretching vibration is particularly sensitive, shifting by up to 80 cm^{-1} in the case of Zn(II) xanthate. The order of shifts for the C-O stretching vibrations of the metal xanthates is $Zn(II) \gg Cu(I) > Pb(II) > Fe(III)$. In the



Fig. 7. HAGIS spectra of (a) Ni(EtOCS₂)₂, (b) Cu(EtOCS₂), (c) Pb(EtOCS₂)₂, (d) Zn(EtOCS₂)₂ and (e) Fe(EtOCS₂)₃ in the region of C-O and C-S stretching vibrations, marking the shift of bands due to variation of the metal. Bands labeled * are due to ethanol.

Table 2

Gas-phase bands observed in the C-C, C-O and C-S region
above Fe(EtOCS ₂) ₃ , Zn(EtOCS ₂) ₂ , Cu(EtOCS ₂), Pb(EtOCS ₂) ₂
and Ni(EtOCS ₂) ₂ , compared with those of the metal xanthates
themselves

Compound	Solid	Gas	
Fe(EtOCS ₂) ₃	1276	1275	
	1257	1245	
	1144	1157	
	1120	1102 ^a	
	1051	1143 ^a	
	1029	1026 ^a	
	1005	1021ª	
	863	867	
	812	798	
$Zn(EtOCS_2)_2$	1222	1274	
	1207		
	1148		
	1123	1103ª	
	1043	1043 ^a	
	1003	1027 ^a	
		1016 ^a	
	915	894	
	865	865	
Pb(EtOCS ₂) ₂	1222	1242	
	1197	1228	
	1144		
	1112	1118	
	1056	1045 ^a	
	1028	1034 ^a	
	1020	1017 ^a	
Ni(EtOCS ₂) ^b ₂	1261	1222	
	1145	1137	
	1123		
	1056		
	1027	1033	
	1002		
	859		
Cu(EtOCS ₂)		1280	
	1201	1221	
	1152	1152	
	1124	1120	
	1050	1072	
	1037	1043	
	1010		
	870	868	
	814	849	

^a Determined by peak fitting using OPUS[®] fitting software to extract information from beneath the ethanol bands.

^b Peak positions approximately ± 10 cm⁻¹ due to difficulty in measurement of very weak bands.

case of Ni(II) xanthate, the bands are so weak that it is difficult to determine the shifts. This point is of interest, as the metals which form discrete metal xanthates, Fe(III) and Ni(II), exhibit the smallest $v(C_1-O)$ shifts on evaporation into the gas phase. Zinc(II), in which the structural change is from a network solid to a discrete gaseous species exhibits the largest $v(C_1-O)$ shift. The frequency of the C₁-O stretch has been related to the strength of the metal-S bond [2](a),(c),(d). If this is true, then Zn(II) strengthens most on transition from solid to gas, as would be expected if a structural change of this type was occurring. Unfortunately, it proved difficult to obtain a gas-phase spectrum of a metal-xanthate complex alone. At a temperature where substantial sublimation occurs, decomposition is also prevalent, masking the gas-phase complex IR spectrum. Another possibility remains that these are mixed xanthato-alkoxy or thioalkyl complexes. However, there is no evidence of alkoxy or thioalkyl bands in the spectrum.

The volatility of the metal xanthates adds several complications to the discussion. Firstly, the question arises as to whether the reaction products come from a gas-phase or a solid-state reaction. If a gas-phase reaction is involved, there should be a correlation between volatility and reaction rate. The more volatile reactants should produce a higher rate constant. This does not appear to be the case. Alternatively, if the metal xanthate complex is volatile, energy transfer from the sample boat to the complex should be less efficient, resulting in a lower effective temperature being experienced by the complex. Although the relative volatility is difficult to measure, this suggestion does appear to apply, although the correlation may be coincidental. In particular, the Ni(II) complex is the most visibly subliming material and is also least reactive.

3.3. Kinetic analysis

The kinetics of these reactions were probed in two separate experiments, involving a representative complex of each group, namely the Zn(II)and Pb(II) xanthates, undertaken by following the behaviour of the gas-phase species with respect to time. At each temperature, the spectra were recorded over a 1 h time interval from the initial thermal equilibration time. The reaction is initially approximately zero order in each of the triatomic gases, as would be expected from the unimolecular extrusion process proposed in this work. Moreover, in the case of Zn(II) xanthate, the calculated activation energies exhibit a very small range, from > 50 to 80 kJ mol⁻¹, effectively equal, for all four species, as required by the assumption of separate mechanistic processes if a constant ratio of products is to be obtained. From the ¹³C-labeling experiment, the reaction is reversible, so it is only pseudo-zero order, following the equation:

$$M(S_2COR) \underset{k_{-1}}{\overset{k_1}{\underset{k_{-1}}{\leftarrow}}} M(OR) + CS_2$$
$$d[CS_2]/dt = k_1 - k_{-1}[CS_2]$$
(1)

Since $[CS_2]$ is very small, at least initially, the reverse reaction is kinetically negligible and so

$$d[CS_2]/dt \approx k_1$$

The low activation energies of these reactions means that, over a 20°C interval, the rate increase is large and the increase in the amounts of the gas-phase species is large compared with that observed over even a long time period. As the amount of the gaseous product increases dramatically at higher temperatures ($>100^{\circ}C$), the reverse reaction becomes significant and the apparent rate of formation of some products decreases. This makes the activation energies determined only approximate, particularly for the generation of COS, the major product. In fact, at 120°C, the concentration of COS decreases with time under this regime. This contrasts with the earlier experiments, where this level of gas generation is never approached, due to the use of a 5 min interval at each temperature as opposed to the 1 h interval in this analysis. A more detailed kinetic analysis of this process is beyond the scope of the present work and is currently in progress. This observation does, however, imply that care must be taken in the qualitative analysis used above to ensure that this high overall gas level does not apply.

For the case of Pb(II) xanthate, the analysis is difficult owing to the small range of temperatures over which some of the products are generated. However, the activation energies determined are in the range $150-310 \text{ kJ mol}^{-1}$, at least twice those for the Zn(II) xanthate decomposition. Moreover, the range of values is over 150 kJ mol⁻¹ compared with only 30 kJ mol⁻¹ for the Zn(II) system. Notably, the reverse reaction does not have a significant influence on the kinetics of the decomposition until a much higher temperature and a much greater concentration of the gas-phase species. Importantly, the concentration of CO₂ does not change with time until > 100°C, implying that its source below this temperature is different from that above the threshold. As noted above, much of the CO₂ probably originates from desorption of the gas from the sample boat, rather than from the decomposition of the xanthate complex. This suggestion is confirmed by the presence of unlabeled CO_2 in the ¹³C-labeling experiment at approximately the same levels as seen in the Pb(II) xanthate decomposition. At higher temperatures, the sublimation of the Pb(II) xanthate also becomes important at the time intervals employed. The concentrations of the other, alkyl-containing species are too low and the IR bands too overlapped for even an approximate analysis of this type to be performed.

A spectroscopic analysis of the solid residues left in the sample boat is complicated by significant variablility. This is due to the difficulty in maintaining a constant level of decomposition. Hence, the residues are a complex mixture of products and intermediates. Further examination of these materials is also in progress.

4. Conclusions

Head-space analysis by gas-phase infrared spectroscopy (HAGIS) is particularly suited to the study of the thermal decomposition pathways of solid species, such as metal xanthates, which generate gaseous species during this process. Metal xanthates decompose thermally in vacuo in the temperature range $25-120^{\circ}$ C, initially and principally by the extrusion of the triatomic gaseous species CS₂, COS and CO₂. The first stage is reversible, hence, the production of CO_2 from a monothiocarbonate intermediate. The metal xanthates fall into two groups; those which decompose readily [Fe(III) and Zn(II)] and leave metal-S bonded residues in the sample boat and those which decompose relatively little and generate more highly oxygenated metal residues [Ni(II), Pb(II) and Cu(I)].

These processes are not at chemical equilibrium and so, reflect the kinetic, rather than thermodynamic states of the system. However, in the case of the first group of metal xanthates, the ratios of products are relatively constant with time and so, the activation energies of all processes are believed to be closely similar. For the second group of metal xanthates, the activation energies are highly variable, making this analysis a kinetic snapshot of the final result. Thermal equilibrium is attained only after long exposure times, making it an impracticable means of analysis.

Other products observed in the gas phase are ethanol, presumably a further decomposition product of the metal alkoxides formed in the initial reaction, and CO, also a secondary product, linked directly to CS_2 production. Another species, which has metal-dependent spectroscopic features, appears consistent with a formulation as gas-phase metal xanthates. The shift of the band due mostly to C_1 -O stretching can be correlated with the extent of structural change required on evaporation of the complex.

Analysis of the gaseous products of the decomposition of $Fe(EtOCS_2)_3$, $Zn(EtOCS_2)_2$, Cu(E $tOCS_2)$, $Pb(EtOCS_2)_2$ and $Ni(EtOCS_2)_2$ by FT-IR spectroscopy provides insights into the mechanisms of the decompositions and forms a basis for the investigation of minerals treated with xanthate collectors. Spectral features due to the presence of metal complexes on the surface can be readily identified.

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