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Thermal analysis of oxamates, thiooxamates and their complexes
Part 1. The ligands

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Abstract

The article describes the thermal behaviour of compounds with general formulae $R_1R_2NCXCOOK$ (R=H, CH_3; X=O,S). The decomposition of oxamates is very complicated with formation of cyanates, cyanides, oxalates and carbonates, the thiooxamates mainly form KOCN, R_2S and CO. The E_a for the decomposition of oxamates is higher than that for the thiooxamates and occurs at higher temperatures. The influence of the crystal structure and the different processes on the E_a values are discussed. © 1998 Elsevier Science B.V.

Keywords: DTA; TG; Thiooxamates; Oxamates; Vibrational spectra

1. Introduction

This study can be regarded as a part of the research into the properties of ligands capable of forming five numbered chelates with divalent metals. The ligands under investigation generally have amide and thioamide functional groups. The substitution of an amide or thioamide function by a carboxylate group makes the molecule still capable to act as a chelate and makes it more important in view of the chemical, biological and applied systems. The synthesis, structure and vibrational characterisation have already been published for the oxamates [1,6] and thiooxamates [2–5,7,8].

A thorough thermal study of these ligands is necessary to collect more information on the similarities and differences in these compounds and their complexes.

2. Experimental

All the compounds under investigation were synthesized according to literature data [1–8]. The infrared spectra were recorded on a Bruker IFS 113 v F.T. spectrometer. The thermal analysis was performed on T.A. Instruments S.D.T. 2960, TGA 2950 and DSC 2920. All experiments were performed under dry nitrogen atmosphere (50 ml/min). The heating rates are stated in the text.

3. Results and discussion

The T_{onset} and the rest masses for the different compounds are given in Table 1. The T_{onset} values were higher for all oxamates compared with the sulphur compounds. The T_{onset} increased from the primary function to the secondary grouping and then dropped for the tertiary amide.

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Table 1
$(\Delta m/\Delta t)_{\max}$ and resultant masses for $R_1R_2NCXCOOK$ (heating rate 5°C/min)

Compound	$(\Delta m/\Delta t)_{\max}$	Resultant mass%	E_a (KJ/mol)
$H_2NCOCOOK$	286	65.8	243
$CH_3HNCOCOOK$	312	62.7	211
$(CH_3)_2NCOCOOK$	280	46.2	225
$H_2NCSCOOK$	180	57.4	160
$CH_3HNCSCOOK$	260	53	175
$(CH_3)_2NCSCOOK$	241	43.6	140

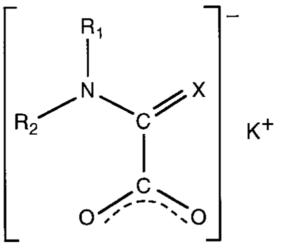

Fig. 1. Molecular geometry of the ligands (R_1,R_2=H or CH_3, X=O or S).

The inductive donating effect of the methyl groups increased the conjugation in the molecule and, consequently, the thermal stability. The lowering, however, observed for the tertiary groups can be explained by the fact that in these molecules we have sterical hindrance between one methyl group (R_2) (Fig. 1) and the carboxylate oxygen, resulting in a non planar configuration for the $(CH_3)_2NCXCOOK$ molecules.

This non planar configuration also obstructs the conjugation and consequently the thermal stability of the compounds. This increased conjugation can normally be proved by a higher νCC mode but for these molecules we observe a very intense and different coupling of the νCC with other groupings, resulting in an unreliable position of the band with the highest νCC character.

The TG, DTA and DTG signals for $CH_3HNCOCOOK$ are given as an example for the oxamates in Fig. 2. From the DTG and DTA signals we can clearly see that the decomposition is not a single process. The resultant products exhibit infrared bands typical for KCN, K_2CO_3, $(KOOC)_2$ and KOCN depending on the heating rate and are well comparable for the three oxamates.

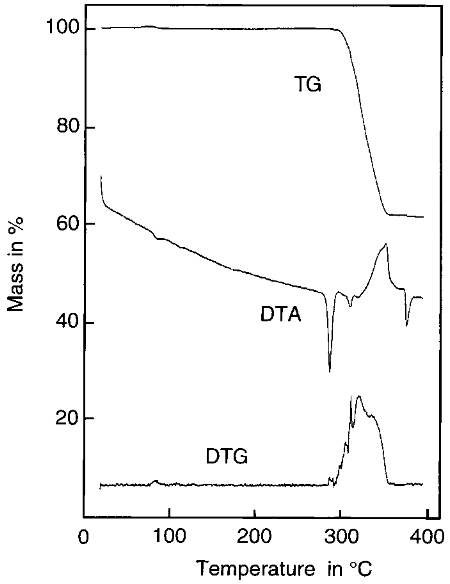

Fig. 2. TG, DTA and DTG for $CH_3HNCOCOOK$.

The decomposition of $H_2NCOCOOK$ was also studied in a KBr matrix. The infrared spectra given in Fig. 3 show that the amide group is first observed by the disappearance of the NH_2-modes and then by the intense $\nu_{as}OCN^-$ at 2170 cm^{-1} in spectrum B. The disappearance of the νCO (amide) at the high frequency side of the $\nu_{as}CO_2^-$ is an added confirmation. The formation of some gaseous CO_2 in the pellet is clear from the band at the high frequency side of the intense nitrile band at 2170 cm^{-1}, as shown in spectrum B. The $\nu_{as}CO_2^-$ and $\nu_sCO_2^-$ were still observed after 15 h and the formation of CO_3^{2-} is clear from the spectrum after 30 h (C). The weak bands on the right frequency side of the intense $\nu_{as}OCN^-$ at 2170 cm^{-1} are pure νCN from nitriles such as KCN. The fact that this decomposition exhibits more than one elemental process can also be observed from the different E_a values [9] as given in Table 2. The comparison of the different E_a values for the oxamates (see Table 1) indicate similar reaction patterns for these molecules.

The TG, DTA and DTG signals for $H_2NCSCOOK$ are given in Fig. 4(A). The decomposition of this compound starts with the formation of H_2S by a highly endothermic process at ca. 180°C and then the formation of CO over a very wide range (180–400°C). The remaining mass (57.4%) practically corresponds to the formation of pure KOCN, and is also indicated

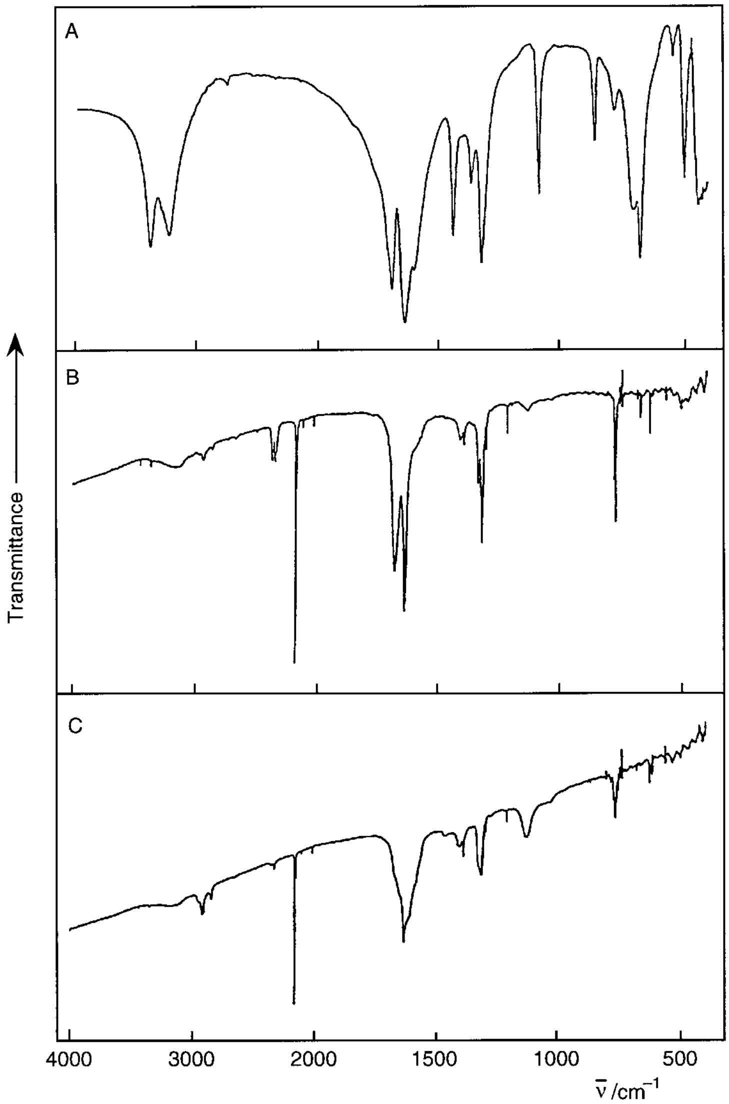

Fig. 3. Infrared spectra of $H_2NCOCOOK$ in KBr matrix. 'A' at room temperature, 'B' after 15 h at 250°C, 'C' after 30 h at 250°C.

by the intense 2170 cm^{-1} band in the infrared spectrum. H_2S gas was confirmed by passing the gas through a dilute $AgNO_3$ solution, as a precipitate of black Ag_2S. The CO gas was identified in a dilute $PdCl_2$ solution by the formation of the black precipitate of metallic Pd.

The TG, DTA and DTG signals for $CH_3HNCSCOOK$ are shown in Fig. 4(B). The higher decomposition compared with $H_2NCSCOOK$ indicate that the decomposition which clearly occurs in different steps for $H_2NCSCOOK$ occurs in one step at higher temperature for the methyl derivative.

Among the different alkyl derivatives, the C_3H_7-derivative should be mentioned as it occurs as a monohydrate where the water is released at very high temperature (185°C), as is clear from the scan given in Fig. 4(C). Fig. 4(B) and (C) clearly show that the decomposition of the monosubstituted thiooxamates strongly depend on the alkyl-substituent.

Table 2
E_a values (KJ/mol) for the decompostion of $CH_3HNCOCOOK$ at different α-values

α	Temperature (°C)				E_a (KJ/mol)
	Heating rates (°C/min)				
	1	5	10	20	
0.1	294.5	307.5	317.5	329	251
0.2	299	312.5	324	336	230
0.3	301	316	328	341	219
0.4	304	320	332	345	216
0.5	306	324	335.5	349	212
0.6	308	326	338.5	352	206
0.7	310	331.25	342	356	200
0.8	311	335	345	360.5	191
0.9	313	340	349.5	367.5	176

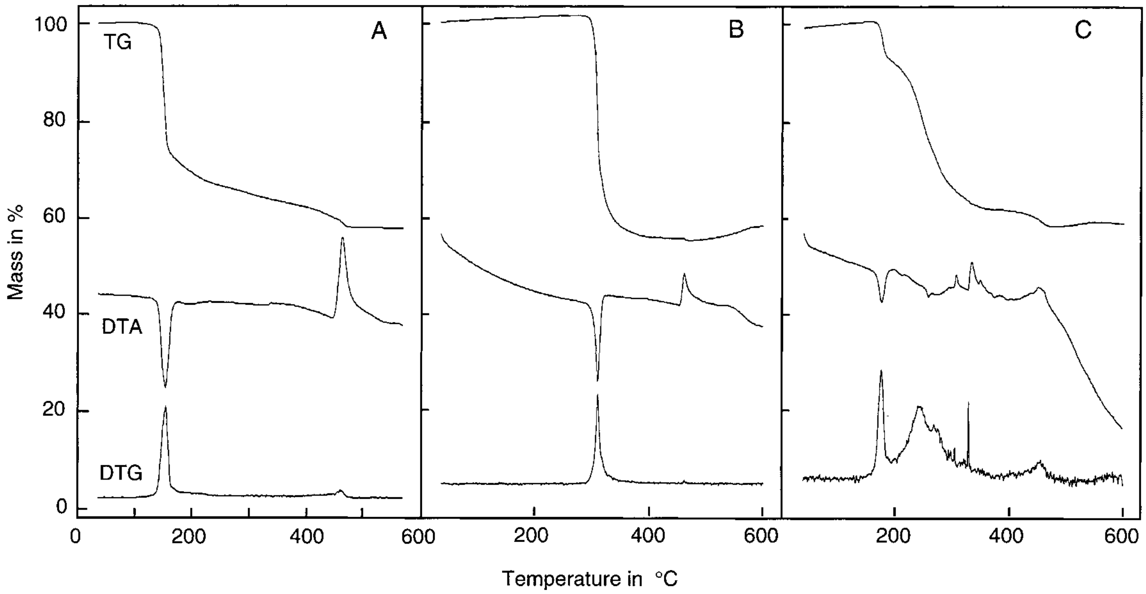

Fig. 4. TG, DTA and DTG for (A) $H_2NCSCOOK$, (B) $CH_3HNCSCOOK$, and (C) $C_3H_7HNCSCOOK{\cdot}H_2O$.

Fig. 5 shows the TG, DTA and DTG curves for $(CH_3)_2NCSCOOK{\cdot}H_2O$. The first endothermal process in the 70°C region is the release of the water molecule from the monohydrate, the loss of weight of 9.6% corresponding to 1 mol of water. The second endothermal process occurs without loss of weight and is ascribed to the melting of the compound. The third endothermal process is the decomposition of the liquid compound with formation of mainly KOCN and KCN.

The E_a values for the dehydration and decomposition of the liquid water-free compound for different heating rates are given in Table 3.

Fig. 6. shows the molecular geometry for the $(CH_3)_2NCSCOOK$ monohydrate [6]. The two functional groups (i.e. the tertiary thioamide and the carboxylate group) can be considered as planar. The dihedral angle between these two planes is ca. 88.3°. The water molecule can be observed from the figure as hydrogen bonded to one oxygen of the carboxylate

Table 3
E_a values for dehydration and decomposition of $(CH_3)_2NCSCOOK{\cdot}H_2O$

α	Dehydration of $(CH_3)_2NCSCOOK{\cdot}H_2O$		Decomposition of $(CH_3)_2NCSCOOK$	
	T_{av} (°C)	E_a (Flynn & Wall) (KJ/mol)	T_{av} (°C)	E_a (Flynn & Wall) (KJ/mol)
0.1	57.1	155	269.3	142
0.2	59.6	146	281.1	138
0.3	61.6	132	287.4	139
0.4	63.6	123	291.5	140
0.5	65.4	115	294.8	141
0.6	67.5	107	297.4	140
0.7	69.5	103	299.5	140
0.8	71.7	98	302.2	138
0.9	73.8	95	305.6	137

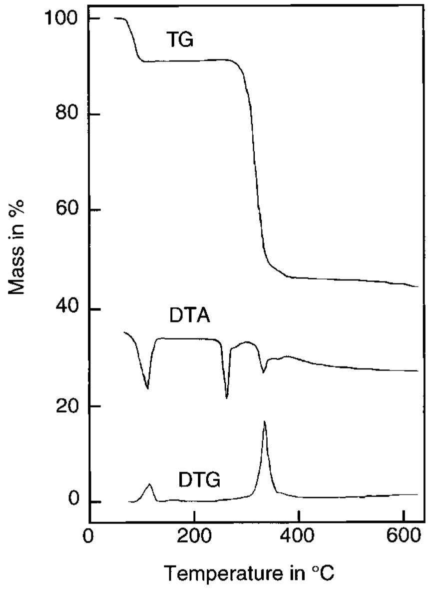

Fig. 5. TG, DTA and DTG for $(CH_3)_2NCSCOOK{\cdot}H_2O$.

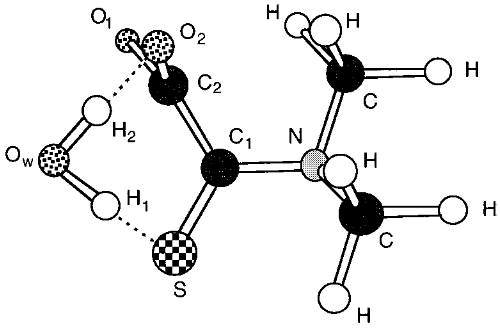

Fig. 6. Molecular geometry of $(CH_3)_2NCSCOOK{\cdot}H_2O$.

group and the sulphur atom of the thioamide function. In order to release the water molecule, the crystal structure and the H_2–O_2 and H_1–S hydrogen bonds must be broken.

The E_a values are for this dehydration ca. 50% higher at low heating rates, due to the energy to break the crystal structure which is consequently more important at lower heating rates.

The similar values obtained for the E_a for the decomposition of the liquid compound prove that this decomposition has the same pathway over the whole process.

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