Thermal Study of Some Metal Ethyl Xanthates

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Abstract

Thermal decomposition studies of metal ethylxanthates of Ca(II), Mn(II), Fe(III), Co(II) and Ni(II), were carried out in dynamic air and dynamic nitrogen atmospheres using simultaneous TG-DTA techniques with a view to compare their thermal behavior. Thermal stabilities of these five metal ethylxanthates in the two atmospheres have been studied, and the thermal stabilities among these metal ethylxanthates have also been compared. Thermal decomposition reactions of these compounds have been suggested in air and nitrogen atmospheres. Among these compounds metal ethyl xanthates show greater thermal stability in air atmosphere than in nitrogen atmosphere. Again it is seen that thermal stability of the metal ethyl xanthates decreases with increase in atomic number.

1. *Introduction*

Solids are the most organized state of matter, and at the same time, they are extremely complex exhibiting a variety of compositional and structural features[1]. Xanthates and their metal derivatives have versatile applications in science and industry. A search through the literature has shown that very limited studies on the thermal bahaviour of metal xanthates have been done. Therefore, it would be worthwhile to carry out systematic studies on the thermal behaviour of some typical metal xanthates with a view to compare their thermal stabilities. Thus, the present investigation is concerned with the thermal decomposition studies of some metal derivatives of ethylxanthate. Study of solid state reactions is one of the most fascinating and emerging research fields in chemistry, as these reactions remain to this day the least understood of the chemical reactions both from dynamic and mechanistic points of view. Real solid state reactions occur in multiple steps that will usually have different kinetic parameters. Information of the kinetics and mechanisms of solid state decomposition is of both practical and theoretical importances[2,3]. New materials such as inorganic superconductors and conducting organic polymers, which exhibit usual electric and magnetic properties, promise to shape the technology of the future[4, 5]. There are three aspects in the study of solid state reactions, *viz.*, the phenomenological, thermodynamic and kinetic aspects. The phenomenological aspect is mainly concerned with the stability ranges, temperatures of decomposition, enthalpy changes and other qualitative and semi-quantitative observations taking place during the reaction. The thermodynamic aspect is related to the initial, final and equilibrium states of the system. The kinetic study is concerned with the determination of rate and mechanism of the decomposition reaction. In the present investigation, the phenomenological aspects of some typical thermal decomposition reactions are studied.

2. *Xanthates*

Xanthate usually refers to a salt with the formula $ROCS_2^-M^+$ (R = alkyl; M+ = Na^+, K^+). The name *xanthates* is derived from Greek , meaning yellowish golden. Most of the xanthate salts are yellow in colour. There is growing interest in the chemistry of sulphur compounds in view of their encouraging anticancer, antiviral and antifungal activities as well as their wide spread industrial applications. Dithiocarbamates, xanthates, dithiolates and dithiophosphates belong to this class of compounds. Among these xanthates are the most versatile sulphur compounds.

Potassium ethylxanthate has strong affinity for transition and non-transition metals, and is used as a chelating agent. Several metal ethylxanthates have been reported, and these have been extensively used as pesticides and vulcanization accelerators[6]. It seems from the literature that thermal decomposition studies of these metal ethylxanthates have not been done so far. As part of a programme for the thermal analysis of solids, some metal ethylxanthaes have been studied using simultaneous TG-DTA techniques. Metal ethylxanthates of Ca(II), Mn(II), Fe(III), Co(II) and Ni(II), have been used for the present investigation. Thermal decomposition studies of these metal ethylxanthaes have been carried out in two distinct atmospheres, *viz.*, in air (an oxidizing atmosphere) and in nitrogen (an inert atmosphere) with a view to compare their thermal behaviours in different environments. The results of these studies are discussed in this work.

3. Basis of Thermal Analysis

The term, thermal analysis (TA) refers to a group of techniques, in which a physical property of a substance is measured as a function of temperature, while the substance is subjected to a controlled temperature programme. In general, these methods are used to measure the changes occurring in the physical properties of a material such as mass variation as a function of temperature.. For thermal analysis the basic parameter necessary is the change in heat content or enthalpy. Any substance can be characterized by its free energy change, (ΔG), *i.e.*,

$$\Delta G = \Delta H - T\Delta S$$

where ΔH denotes the change in heat content and ΔS is the change in entropy at temperature, T. Every system has a tendency to attain a state, in which the free energy is the minimum at a given temperature.

All these transformations are characterized by the temperature at which the transformation occurs and by a change in heat content as manifested by an increase or decrease in the temperature, depending on whether the reaction is exothermic or endothermic, respectively. This is the basis of differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The change in heat content is sometimes accompanied by a change in mass and the observation of such a change is the basis of thermogravimetry (TG).

4. Thermal Decomposition Studies of Metal Xanthates

Thermal stability of nickel(II) alkylxanthates is best described as moderate since all decompose initially to NiS at relatively low temperatures and NiO as the final product[6]. A thermal decomposition mechanism for the nickel(II) alkylxanthates involving carbonyl sulphide, nickel(II) sulphide and S-ethyl O-ethyl xanthate as stable intermediates has been confirmed by mass spectrometry. From thermogravimetric data and volatilization characteristics the nature of the terminal alkyl group attached to the xanthate moiety considerably influences the thermal stability of these compounds. Khwaja *et al* have reported detailed TG data of arsenic(III), antimony(III) and bismuth(III) alkylxanthates, $[ROCS_2]_3M$, where R = methyl, ethyl, isopropyl, n-butyl, cyclohexyl and benzyl, and proposed a general thermal decomposition mechanism for these complexes involving carbonyl sulphide, carbon disulphide, olefins and the metal sulphide as stable intermediates. Thermal degradation of the arsenic, antimony and bismuth complexes reveals the absence of stable intermediates of the type, ROCSSR. Hence, the thermal decomposition mechanism of a particular metal alkylxanthate appears to depend up on both the nature of the R-group and the coordinated metal[7]. Thermal decomposition studies of ethylxanthato complexes of iron(III) and nickel(II) have been carried out by Natu *et al*[8]. The xanthates appear to be suitable for studying the formation of metal sulphides and/or oxides because of their low decomposition temperatures compared with other complexes. Thermal decomposition of addition compounds of bis (ethylxanthato)nickel(II), which is a diamagnetic square planar complex has been studied and shows the loss of trapped solvent (ether) followed by the loss of the addendum leaving behind the parent xanthate complex[9]. Pandey has studied the thermal behaviour of zirconiium(IV) alkylxanthate[10].

5. Experimental

The metal ethylxanthates mentioned were prepared by a common procedure[11,12]. Each of the metal salts and /potassium ethylxanthate were dissolved separately in water, and these solutions were mixed together in 1:2 mole ratio (for Fe derivative 1:3 ratio) with stirring. The metal derivative precipitated in each case was filtered and dried *in vacuo* over phosphorus(V) oxide. The TG, DTG and DTA curves of these metal ethylxanthates were recorded on a Mettler Toledo STARe thermal analysis system in air and nitrogen atmospheres with a heating rate of $10^0C\ min^{-1}$ and a sample mass of ~3 mg in the temperature range 30 - 800^0C. The plateaus in the TG curves, and the peak temperatures and the peak width in the DTG and DTA curves were tabulated.

The final residue obtained in each case was identified by performing the pyrolysis experiment in air or in nitrogen, as the case may be, and the residue was identified by chemical analysis. The mass losses obtained from the TG curves and the pyrolysis experiments were compared with the theoretical values. All the metal derivatives of ethylxanthates prepared for the present investigation were analyzed for their metal contents by standard methods[8]. A known amount of the sample (~0.2 g) was treated with 10 mL of concentrated nitric acid and 5 mL of 5 % (V/V) of bromine in carbon tetrachloride in a beaker. It was then heated on a boiling water bath to dryness, the residue was treated with concentrated hydrochloric acid (10 mL) and heated to dryness on the boiling water bath. The residue obtained was dissolved in water, which was used for the determination of metal content of each of the samples as described[8].

6. Results and Discussion

The plateaus in TG curves, peak temperatures and peak widths in DTG and DTA curves are presented in Tables 1 and 2. These values are obtained from the TG, DTG and DTA curves of the above mentioned metal ethylxanthates. Two sample curves of calcium and nickel ethyl xanthates are shown in figures 1 to 4. The phenomenological aspect of the thermal decomposition of the metal ethylxanthates is discussed.

Five metal derivatives of,Ca(II) Mn(II), Fe(III), Co(II), Ni(II), have been studied using simultaneous TG/DTA techniques in two distinct atmospheres – air and nitrogen with a view to compare their thermal behaviour. The TG, DTG and DTA curves of all the five compounds were recorded in the temperature range, 30-800^{0}C using a heating rate of 10^{0}C min^{-1} and a sample mass of ~3 mg. All the five metal ethylxanthaes studied are anhydrous. The phenomenological aspects of the thermal decomposition of these compounds were studied in detail. Among the five metal ethylxanthates studied, those of Ca(II) exhibit remarkably very high stability in both air and nitrogen atmospheres, while those of Ni(II) exhibit the least thermal stability. Ethylxanthates of Mn(II) exhibit next high stability among the five compounds studied. The Fe(III) salts show medium stability followed by Co(II) .

Among the five metal ethylxanthates studied, they have the following stability order in air (the temperatures of stability are given in parentheses).

Ca	>	Mn	>	Fe	>	Co	>	Ni
(600^{0}C)		(420^{0}C)		(220^{0}C)		(170^{0}C)		(160^{0}C)

The final residues obtained in air are their respective metal oxides. The stability order in nitrogen atmosphere is slightly different than that found in air. The stability order in nitrogen atmosphere is as follows (the temperatures of stability are given in parentheses).

Ca	>	Mn	>	Fe	>	Co	>	Ni
(600^0 C)		(400^{0}C)		(180^{0}C)		(160^{0}C)		(160^{0}C)

Among the five metal ethylxanthates studied ,two of them, *viz*. Ca(II) and Fe(III) decompose in single stage, and the remaining three *viz*., those of , Mn(II), Co(II), Ni(II), decompose in two stage in the air. In nitrogen atmosphere, four of the five metal ethylxanthates, *viz*., those of Ca(II), Fe(III), Co(II), Ni(II) undergo decomposition in single stage, while Mn(II) compound decompose in two stages.

7. Conclusion

The five metal ethylxanthates studied in two atmospheres, *viz*., air and nitrogen behave differently. The salient features of the decomposition reactions in two atmospheres are summarized below.

1. Out of the five metal ethylxanthates studied, two of them, *viz*., those of Ca(II) and, Fe(III) decomposed in single stage, and the remaining three, *viz*., those of Mn(II), Co(II),and Ni(II), decomposed in two stage in the air. In nitrogen atmosphere, four of the five metal ethylxanthates, *viz*., those of , Ca(II), Fe(III), Co(II),and Ni(II), undergo decomposition in single stage, while Mn(II) decompose in two stages.
2. The Ca(II),an Ni(II) ethylxanthates decompose at the same temperatures in air and nitrogen atmospheres.
3. Generally, metal ethylxanthates show greater thermal stability in air atmosphere than in nitrogen.
4. The Mn(II) derivative shows second higher thermal stability in air.
5. Generally, the compounds give the respective metallic oxides in air and metal sulphides in nitrogen atmosphere as the final decomposition residues.
6. The Ca(II) derivative show remarkably high stability in both the atmospheres.
7. The thermal stability of the metal ethyl xanthates decreases with increase in atomic number.

Table 1: Thermal Analysis Data of Metal Ethylxanthates in Air

Compound	Plateau in TG (^{0}C)	Peak in DTG (^{0}C)	Peak width in DTG (^{0}C)	Peak in DTA (^{0}C)	Peak width in DTA (^{0}C)	Mass loss (%)			Residue
						TG	Pyrolysis	Calculated	
Ca(xe)$_2$	Upto 600 After 720	718	600-720	716	600-720	80.7	80.5	80.6	CaO
Mn(xe)$_2$	Upto 420 500-700 After 760	485 745	420-500 700-780	440 730	420-460 700-760	71.1 76.8	--77.1	70.7 76.1	MnS MnO
Fe(xe)$_3$	Up to 220 After 300	273	220-300	271	260-300	61.7	61.1	61.9	Fe$_2$O$_3$
Co(xe)$_2$	Upto 170 200-700 After 780	181 751	170-200 700-780	187 760	180-200 740-780	70.1 72.9	--72.1	69.8 72.4	CoS Co$_2$O$_3$
Ni(xe)$_2$	Upto 160 200-700	190 722	160-200 700-740	197 720	180-210 700-730	69.7 75.1	--75.2	69.1 75.4	NiS NiO

Table 2: Thermal Analysis Data of Metal Ethylxanthates in Nitrogen

Compound	Plateau in TG (^{0}C)	Peak in DTG (^{0}C)	Peak width in DTG (^{0}C)	Peak in DTA (^{0}C)	Peak width in DTA (^{0}C)	Mass loss (%)			Residue
						TG	Pyrolysis	Calculated	
Ca(xe)$_2$	Upto 600 After 740	716	600-740	720	700-730	74.5	74.7	74.4	CaS
Mn(xe)$_2$	Upto 400 500-700 After 760	465 733	400-500 700-760	480 730	460-500 700-740	42.1 70.2	 70.4	42.4 70.7	Mn(SCN)$_2$ Mn$_2$S
Fe(xe)$_3$	Upto 180 After 260	202	180-260	198	180-220	78.8	78.6	79.5	FeS
Co(xe)$_2$	Upto 160 After 220	189	160-220	185	180-210	75.1	75.4	75.2	CoS
Ni[Xe]$_2$	Upto 160 After 200	187	160-200	194	180-220	70.1	69.8	69.7	NiS

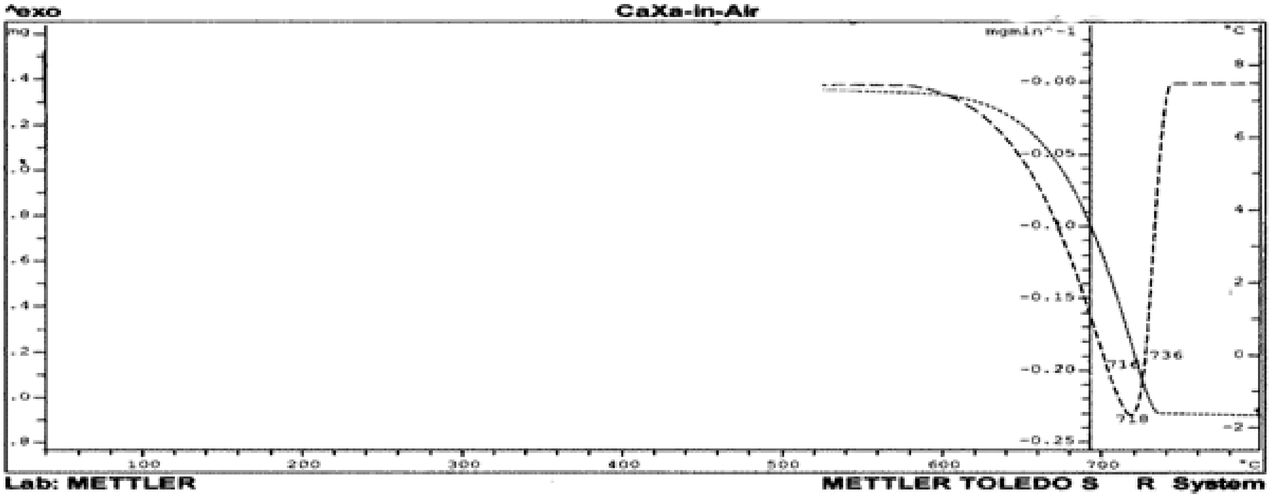

Figure 1: Calcium ethyl xanthate in Air

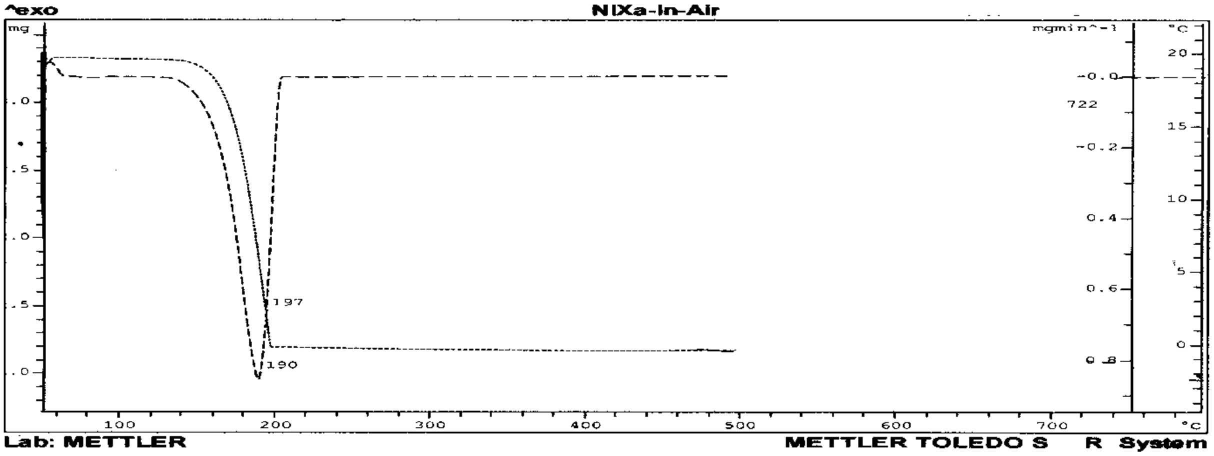

Figure 2: Nickel ethyl xanthates in air

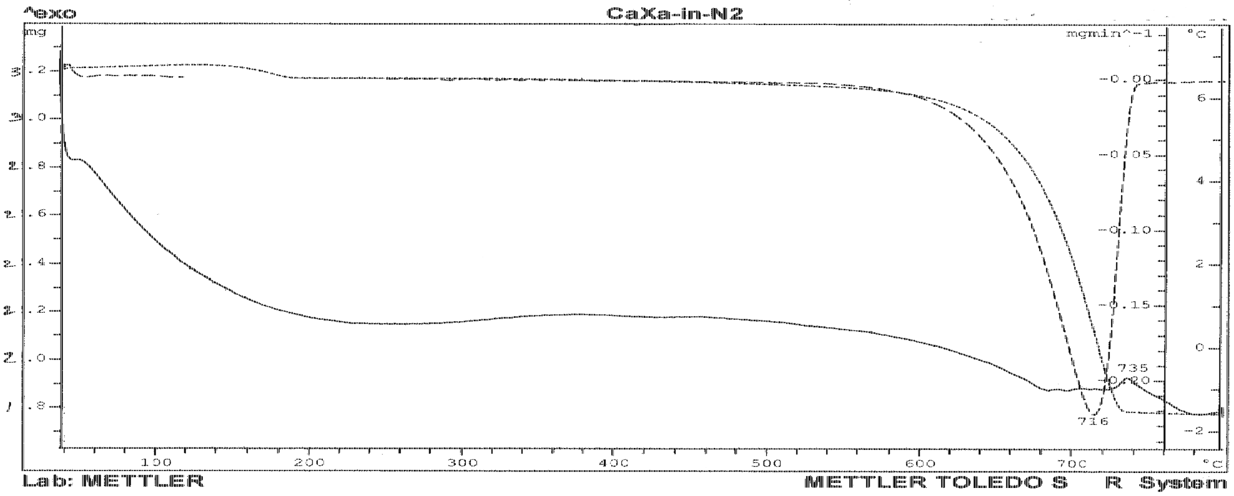

Figure 3: Calcium ethyl xanthate in nitrogen

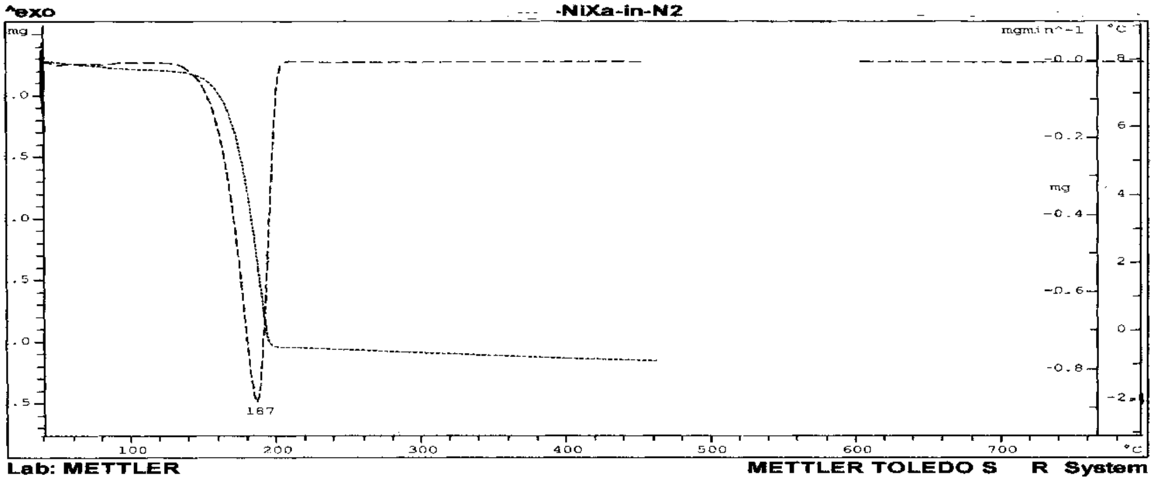

Figure 4: Nickel ethyl xanthate in nitrogen

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