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CHEMISTRY AND MECHANISM OF THERMAL DEGRADATION REACTIONS OF ZIRCONIUM(IV) ALKYL XANTHATE COMPLEXES

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ABSTRACT

The xanthato complexes of zirconyl(IV) $ZrO(S_2COR)_2$ $2H_2O$ ($R = CH_3$, C_2H_5 or C_3H_7) were prepared in aqueous medium and characterized by elemental analysis, conductance, magnetic susceptibility measurements and infrared spectral data The thermal behaviour of these compounds under non-isothermal conditions was investigated by thermogravimetric, derivative thermogravimetric and differential scanning calorimetric techniques in air and N_2 atmospheres It was observed that thermal stability of complexes increases as the chain length of the terminal R group of the xanthate moiety increases, kinetic parameters such as apparent activation energy and order of reaction were determined by the graphical method of Coats and Redfern Heats of reaction for the decomposition steps were calculated from the DSC curves

INTRODUCTION

In recent years, there has been growing interest in the preparation of metal complexes of higher coordination number with nitrogen, oxygen and sulphur donor ligands [1,2] The xanthate ligands, by virtue of their low charge and relatively small bites (~ 3 Å), are well suited for stabilization of higher coordination states [3–5] The general and analytical chemistry of metal xanthates has been comprehensively reviewed by Ramachandra Rao [3] However, apart from the work of Sceney et al on palladium xanthates [6], Cavell et al on nickel xanthates [7] and Khwaja et al on the Group VB metal xanthates [8], data on the thermal decomposition mechanisms of these species are sparse Of interest is the fact that the Group VB metal xanthates show a rather different mechanism of thermal breakdown from those of nickel and palladium Further, no literature has appeared on the kinetics of the thermal decomposition reactions In the present communication, we discuss the preparation, characterization and thermal decomposition of zirconyl(IV) xanthato complexes in nitrogen and oxygen atmospheres

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EXPERIMENTAL

All the reagents used for the preparation of these compounds were either BDH, AnalaR or E Merck grade Potassium salts of alkyl xanthates were prepared as mentioned in the literature [3]

Preparation of the compounds

The complexes were prepared by mixing an aqueous solution of zirconyl chloride with an aqueous solution of the appropriate ligand in a 1 2 molar ratio The solution was refluxed for one to three hours, white- or light brown-coloured precipitate appeared The precipitate was thoroughly washed with distilled water and dried under vacuum over phosphorous pentoxide at room temperature The yield was 62–70%

Analyses

Estimation of the carbon and hydrogen contents were carried out at the Central Drug and Research Institute The metal contents was determined by a standard method as its oxide [9] The sulphur was estimated as $BaSO_4$

Physical measurements

Infrared spectra of the compounds were recorded in the 4000–200 cm^{-1} region with a Perkin Elmer 621 grating spectrophotometer Magnetic susceptibility measurements were carried out on a Gouy's balance at room temperature using mercury tetrathiocyanatocobaltate(II) ($X_g = 16\ 44 \times 10^{-6}$ c g s unit) for calibration

TG and DTG curves were recorded simultaneously on a Setaram G-70 Thermoanalyser (Lyon, France) with sample size 26–36 mg, heating rate 8 K min^{-1} and flow rate of gas 10 cm^3 min^{-1} The DSC curves were recorded on a Perkin Elmer differential scanning calorimeter model DSC-1 in the temperature range 273–773 K in a nitrogen atmosphere only, using about 10 mg sample mass The volatile decomposition products were characterized by mass spectrometry and the solid intermediates were isolated and characterized by analysis and infrared spectra

RESULTS AND DISCUSSION

The method used for the preparation and isolation of these compounds yields materials of high purity as can be judged by elemental analyses (Table 1) and infrared spectral studies

TABLE 1

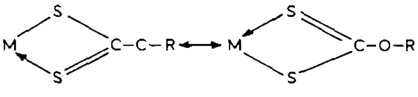
Analytical data of xanthato complexes and their intermediate products resulting at various thermal decomposition steps

Compound	Experimental (Calculated) (%)			
	C	H	S	Zr
$ZrO(S_2COCH_3)_2\ 2H_2O$	13.3	2.6	35.6	25.5
	(13.4)	(2.8)	(35.0)	(25.5)
$ZrO(S_2COCH_3)_2$ (in N_2)	14.7	1.9	39.6	28.8
	(14.9)	(1.9)	(39.8)	(28.4)
$ZrO(S_2COCH_3)_2$ (in O_2)	14.8	1.8	39.6	28.3
	(14.9)	(1.9)	(39.8)	(28.4)
ZrS_2 (in N_2)	–	–	41.0	58.6
			(41.2)	(58.8)
ZrS_2 (in O_2)	–	–	41.1	58.4
			(41.2)	(58.8)
ZrO_2 (in O_2)	–	–	–	73.8
				(74.0)
$ZrO(S_2COC_2H_5)_2\ 2H_2O$	18.5	3.2	33.0	23.7
	(18.7)	(3.6)	(33.2)	(23.7)
$ZrO(S_2COC_2H_5)_2$ (in N_2)	20.3	2.7	36.5	26.0
	(20.6)	(2.9)	(36.6)	(26.1)
$ZrO(S_2COC_2H_5)_2$ (in O_2)	20.5	2.6	36.6	26.1
	(20.6)	(2.9)	(36.6)	(26.1)
ZrS_2 (in N_2)	–	–	41.1	58.4
			(41.2)	(58.8)
ZrS_2 (in O_2)	–	–	41.0	58.6
			(41.2)	(58.8)
ZrO_2 (in O_2)	–	–	–	73.6
				(74.0)
$ZrO(S_2COC_3H_7)_2\ 2H_2O$	23.0	4.2	31.0	21.8
	(23.2)	(4.3)	(31.0)	(22.0)
$ZrO(S_2COC_3H_7)_2$ (in N_2)	25.2	3.4	33.8	24.0
	(25.4)	(3.7)	(33.9)	(24.2)
$ZrO(S_2COC_3H_7)_2$ (in O_2)	25.2	3.7	33.6	24.2
	(25.4)	(3.7)	(33.9)	(24.2)
ZrS_2 (in N_2)	–	–	41.1	58.7
			(41.2)	(58.8)
ZrS_2 (in O_2)	–	–	41.2	58.5
			(41.2)	(58.8)
ZrO_2 (in O_2)	–	–	–	73.6
				(74.0)

The compounds are obtained in crystalline form and are insoluble in common organic solvents, e.g. methanol, ethanol, benzene, acetone or chloroform. They are soluble in dimethylformamide and dimethylsulphoxide. Conductance measurements in dimethylformamide showed that they are essentially non-electrolytes. They are stable as solids in air for a long time. Magnetic susceptibility measurements show that they are all diamagnetic.

Infrared spectral studies

The important infrared frequencies are given in Table 2 The subject of chief interest in the preparation of these complexes is the attachment of xanthate ligands Xanthate can behave as monodentate or bidentate ligand However, assignment of structures of metal xanthates from infrared is not always reliable All the xanthate ligands exhibit four characteristic bands around 1250, 1100, 1060 and 550 cm^{-1}, which according to Watt and McCormick [10] are assigned to $\nu(C{=}S)$, $\nu(C-S)$, $\nu(C-O)$ and $\nu(R-O)$ vibrations These bands are highly coupled and sensitive to the environmental changes A normal coordinate analysis of nickel(II) ethyl xanthate by Agarwala et al [11] indicated that 1250 cm^{-1} band has about 90% contribution from C–O–R stretch and 10% from C=S stretch The band around 1100 cm^{-1} is mainly a contribution of C=O, R–O and C=S stretching modes The band around 1060 cm^{-1} has a single major contribution of 60% from C=S stretch From a detailed investigation of IR spectra of various xanthate derivatives, Little et al [12] also assigned the band at 1070–1060 cm^{-1} to $\nu(C{=}S)$ and proposed that the resonance forms (a) and (b) describe the most probable structure of metal xanthates, which was further supported by Chatt et al [13]



(a) (b)

In our complexes, the C=S stretching band appears at about 1040–1030 cm^{-1} The lowering of the frequency of the C–S band ($\sim$ 30–20 cm^{-1}) in zirconyl(IV) complexes compared with free ligands indicates involvement of sulphur in bonding with the metal The bands observed around 800 and 400–350 cm^{-1} in the IR spectra of complexes may be assigned [14] to $\nu(Zr{=}O)$ and $\nu(Zr-S)$ vibrations In addition, all complexes show a broad band at about 3400–3350 cm^{-1}, assignable to $\nu(OH)$ of lattice water molecules

TABLE 2

Characteristic IR spectral bands (cm^{-1})

Complex	$\nu(C-O-C)$	$\nu(C-O)$	$\nu(C{=}S)$	$\nu(R-O)$	$\nu(Zr{=}O)$	$\nu(Zr-S)$
$ZrO(S_2COCH_3)_2\ 2H_2O$	1250 sb	1150 sb	1030 s	530 s	800 m	350 w
$ZrO(S_2COC_2H_5)_2\ 2H_2O$	1230 sb	1140 sb	1030 s	510 m	790 m	370 m
$ZrO(S_2COC_3H_7)_2\ 2H_2O$	1235 sb	1165 sb	1040 s	525 m	800 m	400 m

Key s = strong m = medium, w = weak, b = broad

Thermal analysis

All these complexes in both nitrogen and oxygen atmospheres show, generally, a two-step weight loss which indicates that the decomposition steps are not significantly influenced by the surrounding gaseous atmosphere employed. There is a qualitative 1 1 correspondence between DSC and DTG curves for all these complexes, indicating that every thermal effect is accompanied by a corresponding mass loss

The first-step weight loss occurs in the temperature range 80–160 ° C and corresponds to loss of water molecules The observed weight losses in the temperature range mentioned above corresponds to two water molecules The expected endothermic behaviour for the dehydration process associated with these compounds has been observed from DSC curves in almost the same temperature ranges The infrared spectra of the products, obtained after dehydration of the complexes, exactly correspond to the original complexes, except that the band around 3400–3350 cm^{-1} vanishes This is due to the absence of water molecules

The second-step weight loss occurs in the temperature range 200–400 ° C and zirconium sulphide is formed at the end of the second decomposition step in the nitrogen atmosphere However, in the oxygen atmosphere, two steps are observed for the decomposition of anhydrous compound At the end of the first step, metal sulphide is formed, which further decomposes in the second step to give zirconium oxide The residues obtained after the endothermic decomposition of anhydrous zirconyl(IV) xanthate complexes has been assigned on the basis of weight loss, far-infrared spectral studies and elemental analysis The infrared spectrum of zirconium sulphide show only one band at *ca* 400–350 cm^{-1}, assignable to $\nu(\mathrm{Zr{-}S})$ The infrared spectra of the products obtained after the decomposition of complexes in the oxygen atmosphere has finished do not show any band at *ca* 400–350 cm^{-1} but instead one band at *ca* 500 cm^{-1} is observed This band is assigned to $\nu(\mathrm{Zr{-}O})$

The volatile decomposition products, which were collected, condensed and analysed by mass spectrometry, are similar to those reported by Cavell et al for nickel alkyl xanthates [7] and Khwaja et al for Group VB metal (As, Sb, Bi) xanthates [8] The TG data for these complexes and mass spectral data for the volatile products of thermal decomposition are consistent with the following thermal decomposition mechanisms

Step I

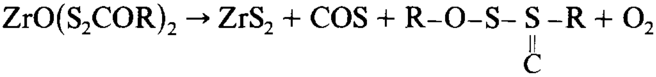
$$\mathrm{ZrO(S_2COR)_2 \cdot 2H_2O} \xrightarrow[-2\mathrm{H_2O}]{80\text{–}160\,^\circ\mathrm{C}} \mathrm{ZrO(S_2COR)_2}$$

TABLE 3

Temperature range, weight loss, activation energy and heat of reaction for different decomposition steps

Decomposition	Temperature range (° C) in N_2 (in O_2)	Percentage weight loss		Heat of reaction (kcal mol^{-1})	Activation energy (kcal mol^{-1})	Order of reaction
		Calc	Found in N_2 (in O_2)			
Decomposition of $ZrO(S_2COCH_3)_2$ $2H_2O$						
1 Dehydration	80–120 (70–120)	10 0	10 2 (9 8)	9 20	–	–
2 Decomposition of anhydrous compound	200–265 (220–290)	51 7	51 5 (51 9)	21 62	40 24	1st
3 $ZrS_2 \rightarrow ZrO_2$ (in O_2)	(380–480)	20 6	– (20 9)	–	–	–
Decomposition of $ZrO(S_2COC_2H_5)_2$ $2H_2O$						
1 Dehydration	108–138 (115–140)	9 3	9 0 (9 2)	18 5	–	–
2 Decomposition of anhydrous compound	280–350 (300–380)	55 5	55 0 (55 8)	20 50	35 80	1st
3 $ZrS_2 \rightarrow ZrO_2$ (in O_2)	(390–470)	20 6	– (20 5)	–	–	–
Decomposition of $ZrO(S_2COC_3H_7)_2$ $2H_2O$						
1 Dehydration	130–160 (120–160)	8 7	8 4 (8 6)	22 8	–	–
2 Decomposition of anhydrous compound	340–400	58 8	58 7 (59 0)	16 32	15 20	1st
3 $ZrS_2 \rightarrow ZrO_2$(in O_2)	(390–480)	20 6	– (20 4)	–	–	–

Step II



$$ZrO(S_2COR)_2 \rightarrow ZrS_2 + COS + R{-}O{-}S{-}\underset{\overset{\|}{C}}{S}{-}R + O_2$$

S-Alkyl, *O*-alkyl xanthate

The TG data for these complexes indicate that the thermal stability of complexes increase as the chain length of the terminal R group of the xanthate moiety increases

Calculation of the apparent activation energy and order of reaction have been performed in nitrogen atmosphere employing the graphical method of Coats and Redfern [15] The plot of $\{-\log[-\log(1-\alpha)/T^2]\}$ versus $1/T \times 10^3$ for $n = 1$ (where n = apparent order of reaction) gives a straight line with slope $-E/2\,303R$ The calculation of the heat of reaction from the DSC curves has been done using the simple expression $\Delta H = KA/m$ where ΔH is the heat of reaction, K is the calibration constant, A is the area under the peak and m is the mass of reactive compound The decomposition temperature ranges, apparent activation energy and heat of reaction for these complexes are given in Table 3

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