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THERMAL STUDIES ON TITANYL, ZIRCONYL AND HAFNYL DITHIOCARBAMATO COMPLEXES

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The dithiocarbamato complexes of titanyl(IV), zirconyl(IV) and hafnyl(IV), abbreviated as $MO(S_2CNRR')_2 \cdot nH_2O$ (M = Ti, Zr or Hf, R = H, R' = C_5H_9; R = H, R' = C_7H_{11}, n = 1 for Ti and n = 2 for Zr and Hf), were prepared in aqueous medium and characterized by elemental analyses, magnetic susceptibility measurements and IR spectral studies. The thermal behaviour of these compounds under non-isothermal conditions was investigated by thermogravimetric, derivative thermogravimetric and differential scanning calorimetric techniques in nitrogen and oxygen atmospheres. The intermediates obtained at the end of various thermal decomposition steps were identified on the basis of analyses and IR spectral studies. Kinetic parameters, such as apparent activation energy and order of reaction, were determined by the graphical method of Coats and Redfern. The heats of reaction for the different decomposition steps were calculated from the DSC curves.

A number of metal dithiocarbamates have been synthesized and characterized in recent years [1–3]. The dithiocarbamate ligand is known to stabilize the higher coordination states of metals due to the low charge and relatively small bites (2.8–2.9 Å). However, a literature survey reveals that, though much work has been carried out on thermal studies of metal dithiocarbamates [4, 5], no paper has appeared on thermal studies of metal oxycation dithiocarbamato complexes, except one for dioxouranium(VI) [6].

In the present paper, we report the thermal behaviour of titanyl, zirconyl and hafnyl dithiocarbamato complexes.

Experimental

The ligands sodium *N*-cyclopentyl- and sodium *N*-cycloheptyldithiocarbamates were synthesized by general methods described in the literature [7].

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Preparation of complexes

The zirconyl(IV) and hafnyl(IV) dithiocarbamato complexes were prepared by the method of Kumar and Kaushik [8]. Titanyl(IV) complexes were prepared by mixing an aqueous solution of potassium titanyl oxalate with the appropriate ligand in 1 : 2 molar ratio. The solution was refluxed for 10–12 hr and then concentrated to one-third of its volume; a cream or light-brown precipitate appeared, which was thoroughly washed with distilled water and dried over phosphorus pentoxide under vacuum at room temperature.

The details on the analyses and physical measurements are the same as reported in the literature [9]. The metal contents were determined by standard methods [10] as their respective oxides.

Results and discussion

The method used for the preparation and isolation of these compounds yielded material of high purity, as can be judged by the satisfactory elemental analysis, IR spectra and thermoanalytical data. The analytical data correspond to those reported by Kumar and Kaushik [8]. The complexes are soluble in dimethylformamide and dimethylsulphoxide, partially soluble in carbon tetrachloride and benzene, and insoluble in other common organic solvents. Magnetic and conductance measurements indicate the diamagnetic and non-electrolyte nature of the complexes. Infrared spectral studies indicate the bidentate nature of the dithiocarbamate ligands, with coordination through sulphur atoms [11].

Thermal analysis

The thermal stability and decomposition ranges of the complexes are given in the Table. Figure 1 shows the DSC curves of these complexes in a nitrogen atmosphere only. There is a qualitative 1 : 1 correspondence between the DSC and DTG curves for all these complexes, indicating that every thermal effect is accompanied by a corresponding mass loss. All the complexes display three-stage weight loss, viz. the dehydration of the complexes, the decomposition of the dehydrated complexes to the respective oxo metal thiocyanates, and finally the decomposition of the oxo metal thiocyanates, in both oxygen and nitrogen atmospheres; the latter shows that the decomposition steps are not significantly influenced by the surrounding gaseous atmosphere employed.

Table 1 Temperature ranges (°C) of thermal decomposition and kinetic parameters

Compound	Decomposition	Temp. range in N_2 (in O_2)	DSC peak temp.	Activation energy, Kcal/mol	Heat of reaction, Kcal/mol	Order of reaction
$TiO(S_2CNRR')_2^a \cdot H_2O$	Dehydration	100–120 (90–120)	110	—	9.40	
	Decomposition of dithiocarbamate	180–240 (170–220)	220	40.24	80.62	Ist
	Decomposition of thiocyanate	400–480 (420–460)	450	—	59.28	—
$ZrO(S_2CNRR')_2^a \cdot 2H_2O$	Dehydration	80–110 (100–110)	100	—	15.80	—
	Decomposition of dithiocarbamate	200–280 (190–250)	240	35.80	10.23	Ist
	Decomposition of thiocyanate	420–500 (420–480)	440	—	21.62	—
$HfO(S_2CNRR')_2^a \cdot 2H_2O$	Dehydration	80–120 (100–130)	90	—	6.68	—
	Decomposition of dithiocarbamate	240–300 (230–300)	230	15.24	48.94	Ist
	Decomposition of thiocyanate	450–520 (450–500)	470	—	7.81	—
$TiO(S_2CNRR')_2^b \cdot H_2O$	Dehydration	100–120 (100–120)	120	—	15.80	—
	Decomposition of dithiocarbamate	200–260 (200–240)	260	35.20	94.22	Ist
	Decomposition of thiocyanate	410–470 (400–470)	480	—	50.12	—
$ZrO(S_2CNRR')_2^b \cdot 2H_2O$	Dehydration	100–130 (100–120)	100	—	10.22	—
	Decomposition of dithiocarbamate	220–300 (220–280)	270	27.12	20.50	Ist
	Decomposition of thiocyanate	450–520 (450–500)	480	—	50.62	—
$HfO(S_2CNRR')_2^b \cdot 2H_2O$	Dehydration	100–120 (100–120)	110	—	10.82	—
	Decomposition of dithiocarbamate	250–300 (230–300)	280	18.72	40.20	Ist
	Decomposition of thiocyanate	450–520 (430–500)	480	—	20.32	—

[a] R = H, R' = C_5H_9; [b] R = H, R' = C_7H_{11}

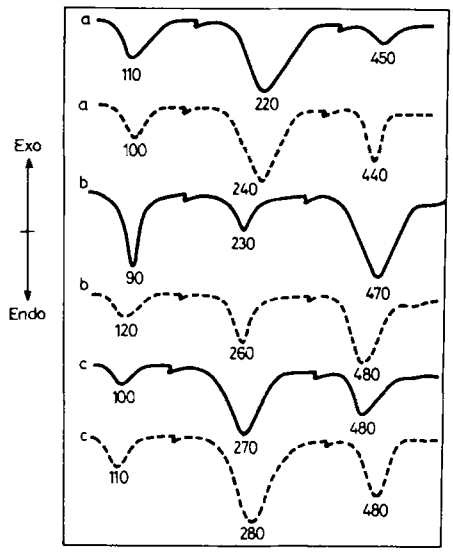

Fig. 1 DSC curves of (a) titanyl (b) zirconyl and (c) hafnyl complexes with *N*-(cyclopentyl)- (———) and *N*-(cycloheptyl) (– – –) dithiocarbamates

1. Dehydration of the complexes

The first weight loss step occurs in the temperature range 80–130° and corresponds to the loss of water molecules. The observed weight losses in this temperature range correspond to one water molecule in the case of the titanyl complexes, and two water molecules for the zirconyl and hafnyl complexes. The expected endothermic behaviour for the dehydration process associated with these compounds was observed in almost the same temperature range in the DSC curves.

2. Decomposition of dehydrated complexes

The second weight loss step occurs in the temperature range 180–300°, the respective oxo metal thiocyanates being formed. This was confirmed via the elemental analysis and the IR spectra. The IR spectra correspond exactly with those reported for titanyl, zirconyl and hafnyl thiocyanates [12, 13]. The thermal decompositions of the dehydrated dithiocarbamato complexes to the respective thiocyanates take place in a single endothermic step.

3. Decomposition of oxo metal thiocyanates

The third weight loss step occurs in the range 480–520° in both nitrogen and oxygen atmospheres. However, the final product at the end of the third step differs in these two atmospheres. In oxygen atmosphere the oxo metal thiocyanates

decompose to give the respective metal dioxides, whereas in nitrogen atmosphere the final products are of indefinite composition. This may be due to the simultaneous decomposition of the metal thiocyanates to the respective metal oxides and sulphides, or to the formation of non-stoichiometric compounds. The formation of metal dioxides as end-products in oxygen atmosphere was confirmed by elemental analysis.

From the above results, the following steps may be proposed for the decompositions of the titanyl, zirconyl and hafnyl complexes:

Step I

$$MO(S_2CNRR')_2 \cdot nH_2O \xrightarrow{80\text{–}130^\circ} MO(S_2CNRR')_2$$

Step II

$$MO(S_2CNRR')_2 \xrightarrow{180\text{–}300^\circ} MO(SCN)_2$$

Step III

In oxygen atmosphere:

$$MO(SCN)_2 \xrightarrow{400\text{–}520^\circ} MO_2$$

In nitrogen atmosphere:

$$MO(SCN)_2 \xrightarrow{450\text{–}500^\circ} \text{indefinite composition}$$

Calculation of the apparent activation energy and order of reaction was performed in nitrogen atmosphere by employing the graphical method of Coats and Redfern [14]. The plot of $\{-\log[-\log(1-\alpha)/T^2]\}$ *vs.* $1/T \times 10^3$ for $n = 1$ (where n = apparent order of reaction) gives a straight line (Fig. 2) with slope $-E/2.303R$.

Calculation of the heat of reaction from the DSC curves was done by 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 calibration constant K was calculated by using the following equation

$$K = \frac{\Delta HmC}{A\Delta T_s}$$

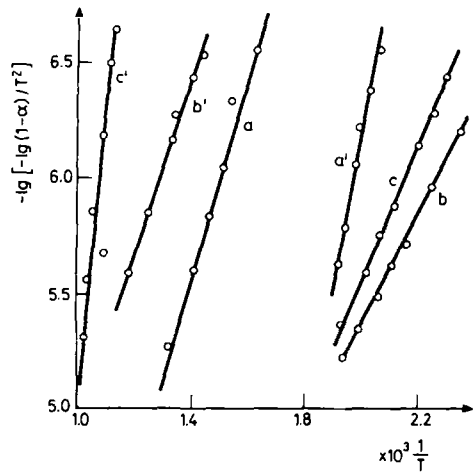

Fig. 2 Coats and Redfern linearization curves for the second step decomposition of titanyl (a, a'), zirconyl (b, b') and hafnyl (c, c') complexes with *N*-(cyclopentyl) dithiocarbamates (a, b, c) and *N*-(cycloheptyl) dithiocarbamate (a', b', c')

where ΔH is the heat of transition in cal/g, m is the mass in mg, C is the chart speed in inch/min, A is the peak area in inch^2 and ΔT_s is the temperature sensitivity in deg/inch. With these units, K is expressed in m cal/min °C. To calibrate the DSC instrument, we chose pure indium metal, the ΔH of which is 6.79 cal/g. The value of K calculated by using the above equation was 148.784 m cal/min deg. The apparent activation energy and heat of reaction in nitrogen atmosphere are given in the Table.

Conclusion

The thermal studies show that the decompositions of the titanyl, zirconyl and hafnyl complexes with *N*-cyclopentyl- and *N*-cycloheptyldithiocarbamates proceed through three major steps: the first is dehydration, the second involves the decomposition of the dehydrated complex to the intermediate oxo metal thiocyanate, and in the last step the thiocyanate decomposes either to metal oxide (in oxygen atmosphere) or to compounds of indefinite composition (in nitrogen atmosphere). The second-stage decomposition in nitrogen atmosphere in all cases follows first-order kinetics. The titanyl complexes are thermally less stable than the corresponding zirconyl complexes, which in turn are less stable than the corresponding hafnyl complexes.

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Zusammenfassung — Die Thiocarbamato-Komplexe von Titanyl(IV), Zirkonyl(IV) und Hafnyl(IV) der allgemeinen Formel $MO(S_2CNRR')_2 \cdot nH_2O$ (M = Ti, Zr oder Hf; R = H, R' = C_5H_9; R = H, R' = C_7H_{11}; n = 1 für Ti und n = 2 für Zr und Hf) wurden in wässrigem Medium hergestellt und durch Elementaranalyse, Messung der magnetischen Suszeptibilität und IR-Spektraluntersuchungen charakterisiert. Das thermische Verhalten dieser Verbindungen unter nicht-isothermen Bedingungen wurde durch TG, DTG und DSC in Stickstoff- und Sauerstoffatmosphäre untersucht. Die nach verschiedenen thermischen Zersetzungsschritten erhaltenen Zwischenprodukte wurden durch chemische Analyse und IR-Spektroskopie identifiziert. Kinetische Parameter, wie die scheinbare Aktivierungsenergie und die Reaktionsordnung, wurden nach der graphischen Methode von Coats und Redfern bestimmt. Für die einzelnen Zersetzungsschritte wurden die Reaktionswärmen aus den DSC-Kurven berechnet.

Резюме — Дитиокарбаматные комплексы титанила, цирконила и гафнила, обозначенные как $MO(S_2CNRR')_2 \cdot nH_2O$ (M = Ti, Zr, Hf, R = H, R^1 = C_5H_9, C_7H_{11}, n = 1 для Ti и n = 2 для циркония и гафния) были получены в водной среде и охарактеризованы элементным анализом, ИК спектрами и измерениями магнитной восприимчивости. Термическое поведение соединений было исследовано в неизотермических условиях методом ТГ, ДТГ и ДСК в атмосфере кислорода и азота. Промежуточные продукты, полученные в конце каждой стадии разложения, были идентифицированы элементным анализом и ИК спектрами. Кажущаяся энергия активации и порядок реакции были определены графически по методу Коутса-Рэдферна. На основе кривых ДСК были вычислены теплоты реакций различных стадий разложения.