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Note

THERMAL STUDIES ON COMPLEXES OF OXOZIRCONIUM(IV) WITH SOME AROMATIC AMINE *N*-OXIDES

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In recent years, a number of complexes of oxozirconium(IV) with oxo-ligands containing X=O groupings, were X = C, N, P, S and As, have been isolated and characterized [1]. But the thermal investigations of these complexes have been carried out to a limited extent. Patel and co-workers have studied oxozirconium(IV) perchlorate complexes with antipyrine [2], pyridine *N*-oxide [3], quinoline *N*-oxide [4], dimethyl sulphoxide [5] and diphenyl sulphoxide [6] by differential thermal studies. Recently, from this laboratory, we have reported some thermal results of oxozirconium(IV) complexes with tetramethylene sulphoxide [7], pyrazolones [8], 2,2′-bipyridyl *N*-*N*′-dioxide [9], 2-methyl pyridine *N*-oxide [10] and 2,2′-bipyridyl mono *N*-oxide [11].

No systematic thermal studies have been reported so far on oxozirconium(IV) complexes of aromatic amine N-oxides. Thus, in the present study, we wish to report the thermal decomposition characteristics of oxozirconium(IV) complexes of pyridine *N*-oxide (pyO), 2,6-lutidine *N*-oxide (LNO) and 1,10-phenanthroline mono-*N*-oxide (phenNO) and their intermediates.

EXPERIMENTAL

The oxozirconium(IV) complexes of pyO [12], LNO [12] and phenNO [13] have been synthesised as reported previously. The technique and instruments used for the thermal studies are reported elsewhere [14].

RESULTS AND DISCUSSION

The thermoanalytical data for the oxozirconium(IV) complexes are presented in Table 1.

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TABLE 1

Thermal data on oxozirconium(IV) complexes of aromatic amine-*N*-oxide

Complex	Decompn. Temp. (°C)		Decompn.-product	TG loss (wt.%)		DTG peak
	Initial	Final		Found	(Calcd.)	
$ZrOCl_2 \cdot 2$ pyO	190	420	$ZrOCl_2$	48.20	(47.02)	Endo
	490	550	ZrO_2	64.30	(63.39)	
$ZrOBr_2 \cdot 2$ pyO	195	425	$ZrOBr_2$	37.80	(37.17)	Endo
	480	550	ZrO_2	72.40	(71.05)	
$ZrO(NCS)_2 \cdot 2$ pyO	160	410	$ZrO(NCS)_2$	42.10	(41.46)	Exo
	465	550	ZrO_2	68.20	(67.71)	
$ZrO(NO_3)_2 \cdot 2$ pyO	200	440	$ZrO(NO_3)_2$	40.40	(40.61)	Endo
	490	550	ZrO_2	69.40	(68.38)	
$ZrO(ClO_4)_2 \cdot 6$ LNO	180	450	$ZrO(ClO_4)_2$	68.80	(67.72)	Exo
	510	605	ZrO_2	88.00	(87.02)	
$ZrOCl_2 \cdot 2$ LNO	210	463	$ZrOCl_2$	59.86	(58.97)	Endo
	490	535	ZrO_2	72.02	(77.99)	
$ZrOBr_2 \cdot 2$ LNO	220	235	$ZrOBr_2 \cdot 0.5$ LNO	33.61	(35.86)	Endo
	235	530	$ZrOBr_2$	43.01	(47.95)	
	530	630		63.52		

$ZrO(NCS)_2 \cdot 2$ LNO	205	430	$ZrO(NCS)_2$	49.86	(48.97)	Exo
	525	605	ZrO_2	72.85	(71.85)	
$ZrO(NO)_3 \cdot 2$ LNO	225	430	$ZrO(NO_3)_2$	50.00	(48.08)	Endo
	535	610	ZrO_2	73.20	(72.35)	
$ZrO(ClO_4)_2 \cdot 3$ phenNO	240	290	$ZrO(ClO_4)_2 \cdot 2$ phenNO	22.66	(21.92)	Exo
	290	330	$ZrO(ClO_4)_2$	66.66	(65.77)	
	590	650	ZrO_2	86.66	(84.24)	
$ZrOCl_2 \cdot$ phenNO	220	330	$ZrOCl_2$	51.33	(52.40)	Endo
	540	640	ZrO_2	86.66	(85.95)	
$ZrOBr_2 \cdot$ phenNO	250	310	$ZrOBr_2$	44.33	(42.33)	Endo
	535	660	ZrO_2	66.66	(62.11)	
$ZrO(NCS)_2 \cdot$ phenNO	230	310	$ZrO(NCS)_2$	45.82	(44.39)	Endo
	530	610	ZrO_2	72.02	(70.64)	
$ZrO(NO_3)_2 \cdot$ phenNO	250	330	$ZrO(NO_3)_2$	46.84	(45.90)	Endo
	540	610	ZrO_2	72.20	(71.19)	

pyO complexes

The differential thermal behaviour of the pyO complex of oxozirconium(IV) perchlorate was investigated by Ramamurthy and Patel [3]. They found the decomposition temperature to be 307°C. In the present work, the TG curves of pyO complexes indicate the absence of water of crystallisation in the complexes and reveals their non-hygroscopic nature. The deligation process of the complexes $ZrOX_2 \cdot 2$ pyO ($X = NO_3$, Cl, Br or NCS) started from ca. 160–200°C and continues up to 440°C, as shown by the break in the TG curves and the peak in DTG curves. The chlorobromo and nitrato complexes decompose endothermically while the thiocyanato complex decomposes exothermically. In the DTG curve a small exo peak occurring at ca. 480°C is due to the oxidation of carbon formed by the decomposition of the complexes. On further heating up to 550°C, the loss in weight corresponds to the formation of ZrO_2 (Table 1) as an end product [9,10].

LNO complexes

The TG and DT analysis of $ZrO(ClO_4)_2 \cdot 6$ LNO shows that the product is hygroscopic in nature. The anhydrous complex is stable up to 180°C, beyond which the decomposition starts and is completed at ca. 450°C. No stable intermediate product is formed in this case. In the DTG curve, one sharp exo peak at 250°C is obtained. At this temperature, the compound decomposes violently with formation of smoke due to the oxygen content of the perchlorate [2,3,8]. A circular exotherm at ca. 490°C is evident due to the oxidation of carbon. At the final stage, ZrO_2 is obtained as an end product. The complex $ZrOCl_2 \cdot 2$ LNO, being very hygroscopic, shows a change in the TG curve at ca. 100°C. The decomposition of the anhydrous complex starts at 210°C and continues upto 463°C, untill all the ligand molecules are removed. Further heating up to 534°C shows the formation of the metal oxide. The complex $ZrOBr_2 \cdot 2$ LNO is thermally more stable than the corresponding chloro complex. The TG analysis of the complex indicates that only 1.5 mole of the ligand is lost at 235°C and complete removal of the ligands occurs at 530°C. Heating up to 630°C produces a weight loss of ca. 63.5%. The composition of the residue should be some intermediate oxidative product of $ZrOBr_2$. The decomposition process of nitrato and thiocyanato complexes is a two step reaction (Table 1). At ca. 600°C the end product is ZrO_2 in both cases [8].

phenNO complexes

Recently, Agarwal et al. [15] investigated the thermal behaviour of 1,10-phenanthroline mono *N*-oxide chelates of thorium(IV) salts. Similar to Th(IV) complexes, the TG and DT curves of oxozirconium(IV) complexes of phenNO indicate that the compounds have no water of crystallisation and are non-hygroscopic in nature. The chloro, bromo, thiocyanato and nitrato complexes decompose endothermically, while the perchlorato complex decomposes exothermically with slight explosion and evolution of smoke. The TG curves show that halide and nitrato complexes complete their decomposition process in two steps. In the first step, both the ligand molecules are lost and in the second step, the metal oxide is formed. No intermediate stable complex has been isolated in these cases. The TG curve of $ZrO(ClO_4)_2 \cdot 3$ phenNO indicates that one molecule of ligand is lost at temperatures up to 290°C, and a stable intermediate compound $ZrO(ClO_4)_2 \cdot 2$ phenNO is obtained. In both cases, the nature of the perchlorate ions is ionic. Further heating of the sample up to 330°C causes the removal of any remaining ligands and finally at 650°C, ZrO_2 is obtained as the end product.

In conclusion, if the minimum TG decomposition temperature is taken as a rough criterion of thermal stability, then the order of stability of the ZrO(IV) complexes with (a) pyO is $NO_3 > Br > Cl > NCS$, (b) LNO is $NO_3 > Br > Cl > NCS > ClO_4$, and (c) phenNO is $NO_3 > Br > ClO_4 > NCS > Cl$.

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