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Thermal Decomposition of Octakis(*p*-dimethylphenylsulfoxide)lanthanide(III) Perchlorates in a Helium Atmosphere*

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In previous work [1–4], we reported on the formation of pure lanthanide oxysulfates, $Ln_2O_2SO_4$, in the thermal decomposition in air of the complexes formed by lanthanide and yttrium perchlorates with sulfoxide ligands. In these studies, unlike previous publications relating to thermal decompositions of metal complexes with these ligands, the products one would expect to obtain from the thermal decomposition of lanthanide perchlorates, *i.e.*, chlorides, oxychlorides and oxides, were not obtained.

In the present work we offer the results of the thermal decomposition of the complexes $Ln(p\text{-}TSO)_8(ClO_4)_3$ (where Ln = Y, Ce, Tb, Dy, Ho, Er, Tm, Yb and Lu and *p*-TSO = *p*-dimethylphenylsulfoxide) in a helium atmosphere, and compare the results with those obtained previously for pyrolysis in air [3].

Experimental

The octakis(*p*-dimethylphenylsulfoxide)lanthanide(III) perchlorates were obtained and characterized by procedures described previously [3, 5].

The thermoanalytical studies were carried out with a Perkin-Elmer TGS-2 thermobalance (T_{max} = 1273 K) and DTA-1700 equipment connected to a 7/4 controller system and a TADS data station. A dynamic helium atmosphere (1 $cm^3\ s^{-1}$) and a heating rate of 033 K s^{-1} were used. α-Al_2O_3 served as a reference material for DTA measurements; both in DTA and in TG studies the amount of complex ranged between 6 and 10 mg.

Results and Discussion

Table I shows the temperature ranges in which appreciable weight losses occurred. It may be seen that all the complexes have similar thermal stability, which in turn is similar to that found when the complexes are decomposed in a dynamic air atmosphere [3]. In this sense they do not start to decompose until temperatures of 475–503 K, close to their melting points, as shown in the onset temperatures of the endothermal peaks recorded in DTA measurements.

Unlike decomposition in air, which occurs in three perfectly distinguishable stages, in helium the decomposition of the complexes takes place in two phases. The first ($T_{initial}$ = 475–503 K and T_{final} = 623–643 K) is similar to that observed at the same temperatures in an atmosphere of air, in which weight losses ranged between 72% for the yttrium complex and 65% for the lutetium complex, and were accompanied by a strong exothermal effect whose temperature maximum, as seen in Table I, is recorded in DTA at between 605 K and 615 K. A second phase that starts at temperatures in the region of 670 K and is maintained until the end of heating, produces a slow and gradual weight loss instead of the two stages found for the same temperature range in the thermal decomposition of these complexes in a dynamic atmosphere of air. This second phase of decomposition of the complexes occurs with a release of energy, as shown by the broad and not very marked exothermal effects recorded in the DTA diagrams between 700 K and the final heating temperature.

In the decomposition in air, we found white residues in proportions theoretically corresponding to lanthanide oxysulfates [3] and CeO_2 when dealing with the residue of the $Ce(p\text{-}TSO)_8(ClO_4)_3$ complex. In the decomposition in helium, the residues at the final heating temperature were black and their X-ray diffraction diagrams permit the identification of the existence of lanthanide or yttrium oxysulfates and of CeO_2 as the only crystalline compounds in the residue; their percentages, as may be seen from Table I, are between 17.4–20.9% of the initial weight of the sample. The difference in weight between both residues has been attributed by us to the formation of carbon, a product of the decomposition of the ligands, which remains stable owing to the lack of sufficient oxygen for its combustion. Thus, when the residues obtained in the calcination of the complexes in a helium atmosphere up to 1173 K are later heated at temperatures between 300 K and 1173 K in a dynamic atmosphere of air, they undergo a single weight loss between 680–900 K, estimated to be 50–60%; this corresponds to 10–11% of the weight of the complex initially considered. Their DTA diagrams point to a single strong exothermal effect whose maximum appears at around 800 K; we attribute this to the combustion of the carbon and its removal from the

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TABLE I. Thermal Data on Octakis(*p*-dimethylphenylsulfoxide)lanthanide(III) and Yttrium Perchlorates in Helium Atmosphere

Complex	Decomposition temperature (K)		Weight residue (%)	DTA temperature (K)
	Initial	Final		
$Y(p\text{-TSO})_8(ClO_4)_3$				492 *endo*
	493	633	28.1	611 *exo*
	663	1173	17.4	733–1173 *exo*
$Ce(p\text{-TSO})_8(ClO_4)_3$				427 *endo*
	475	625	32.4	606 *exo*
	660	1173	18.3	700–1173 *exo*
$Tb(p\text{-TSO})_8(ClO_4)_3$				495 *endo*
	495	633	31.6	615 *exo*
	678	1173	20.5	743–1173 *exo*
$Dy(p\text{-TSO})_8(ClO_4)_3$				493 *endo*
	498	638	32.1	609 *exo*
	673	1173	20.0	743–1173 *exo*
$Ho(p\text{-TSO})_8(ClO_4)_3$				496 *endo*
	498	633	31.9	613 *exo*
	673	1173	20.6	738–1173 *exo*
$Er(p\text{-TSO})_8(ClO_4)_3$				497 *endo*
	499	638	31.3	606 *exo*
	668	1173	20.7	743–1173 *exo*
$Tm(p\text{-TSO})_8(ClO_4)_3$				493 *endo*
	498	638	31.8	615 *exo*
	683	1173	20.9	748–1173 *exo*
$Yb(p\text{-TSO})_8(ClO_4)_3$				498 *endo*
	503	643	32.4	613 *exo*
	693	1173	20.9	743–1173 *exo*
$Lu(p\text{-TSO})_8(ClO_4)_3$				483 *endo*
	483	623	34.6	605 *exo*
	673	1173	20.6	739–1173 *exo*

residue in the form of CO_2. Following this loss of weight the residues are stable and by XRD [6] and IR spectroscopy [7] they have been identified as lanthanide oxysulfates and cerium dioxide. Moreover, the weight percentages observed coincide with those calculated theoretically for the quoted compositions of the residues.

The IR spectra conducted on the gaseous products originating in the decomposition of these complexes up to temperatures in the 630–670 K range and condensed at room temperature, reveal the bands assigned to *p*-TSO, together with three bands of medium intensity at 1320, 1150 and 500 cm^{-1} that point to the partial oxidation to the corresponding sulfone. Similarly, the IR spectra of the solid residues up to temperatures in the 630–670 K range show all the active absorptions corresponding to the sulfate ion in the hydrated lanthanide(III) sulfates. These results are the same as those found for the decomposition of the complexes in air [3].

The X-ray diffraction diagrams performed on $Ce(p\text{-TSO})_8(ClO_4)_3$ heated in helium at temperatures between 900 K and 1100 K, in spite of showing few reflections, reveal the existence of CeO_2 in them (reflections at 312.4, 191.2 and 163.2 pm) and a little $Ce_2(SO_4)_3$ (550, 301 and 285 pm) [8]. The X-ray diffraction diagrams of the remaining complexes present the characteristic lines of lanthanide oxysulfates, although fewer in number and less well-defined than those found when the samples are the residues of calcination of the complexes at 1173 K. Moreover, the diagrams reveal the presence of other lines corresponding to reflections with angles of less then 40 °; these are comparable to the diffraction patterns of the anhydrous sulfates of yttrium [9] and lutetium [8].

Analysis of the products, their stoichiometry and the relative rate of decomposition with respect to that occurring in air allow us to conclude that the thermal decomposition of these complexes in a helium atmosphere occurs accompanied by the formation of the following products.

Between 475 K and 640 K:

$$2\mathrm{Ln}(p\text{-}\mathrm{TSO})_8(\mathrm{ClO}_4)_3 \longrightarrow \mathrm{Ln}_2(\mathrm{SO}_4)_3\cdot x\mathrm{H}_2\mathrm{O} + y\mathrm{C} \quad (x \simeq 15, y \simeq 42)$$

Between 663 K and 1173 K for Ln = Tb–Lu and Y:

$$\mathrm{Ln}_2(\mathrm{SO}_4)_3\cdot x\mathrm{H}_2\mathrm{O} + y\mathrm{C} \longrightarrow \mathrm{Ln}_2\mathrm{O}_2\mathrm{SO}_4 + z\mathrm{C} \quad (z \simeq 40)$$

and

$$\mathrm{Ce}_2(\mathrm{SO}_4)_3\cdot x\mathrm{H}_2\mathrm{O} + y\mathrm{C} \longrightarrow \mathrm{CeO}_2 + z\mathrm{C}$$

This requires that not all the sulfoxide ligands be eliminated and that they must be present in the residues, stabilizing the lanthanide ions as sulfates, which, in the presence of the carbon from the decomposition of part of the ligands, are slowly converted into oxysulfates (or cerium dioxide) from temperatures of about 730 K onwards.

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