Thermochimica Acta, 146 (1989)381–383
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

THERMOGRAVIMETRIC STUDIES OF HEXAMETHYLPHOSPHORAMIDE (HMPA) LANTHANOID PERRHENATE COMPLEXES

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(Received 29 November 1988)

HMPA lanthanoid perrhenate complexes with compositions $[Ln(ReO_4)_2(HMPA)_2]ReO_4$ (Ln = La–Nd) and $[Ln(ReO_4)_2(HMPA)_4]ReO_4$ (Ln = Sm–Lu, Y) have been recently described [1]. In this note a TG study of these compounds is presented.

EXPERIMENTAL

The TG curves were determined under nitrogen atmosphere in a Perkin–Elmer TGS-1 system, with sample weights varying from 0.70 to 0.95 mg at a heating rate of 10 K min^{-1} (see Fig. 1 for some representative curves).

RESULTS AND DISCUSSION

The compounds behave as 1 : 1 electrolytes in nitromethane and acetonitrile. Splittings and shifts of ν(PO) are attributed to, at least, non-equivalent PO groups. IR spectra give evidence of non-coordinated and bidentate perrhenate for the lighter lanthanides and non-coordinated and monodentate perrhenate for the heavier ones. Spectroscopic parameters obtained from the neodymium compound absorption spectrum indicate a very small covalent character. The fluorescence spectrum was interpreted in terms of a C_{4v} symmetry for the $Ln(O)_6$ chromophore.

An analysis of the TG data reveals that under the experimental conditions used, three different decomposition schemes exist, depending on the rare-

0040-6031/89/$03.50

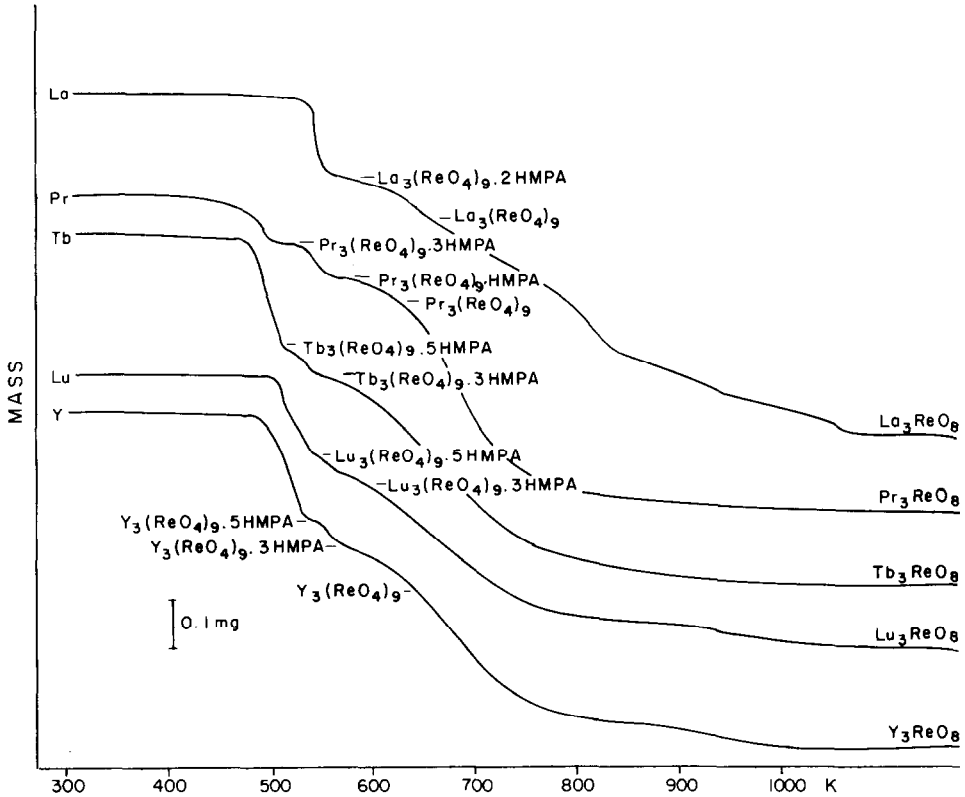

Fig. 1. Thermogravimetric curves for some representative complexes.

earth ion:

$$
\begin{aligned}
&3\{[La(ReO_4)_2(HMPA)_2]ReO_4\} \rightarrow \\
&3\{[La(ReO_4)_2(HMPA)_{2/3}]ReO_4\} + 4HMPA \rightarrow \\
&3\{[La(ReO_4)_2]ReO_4\} + 2HMPA \rightarrow \\
&La_3ReO_8 + 4Re_2O_7
\end{aligned}
\qquad (1)
$$

$$
\begin{aligned}
&3\{[Ln(ReO_4)_2(HMPA)_2]ReO_4\} \rightarrow \\
&3\{[Ln(ReO_4)_2(HMPA)]ReO_4\} + 3HMPA \rightarrow \\
&3\{[Ln(ReO_4)_2(HMPA)_{1/3}]ReO_4\} + 2HMPA \rightarrow \\
&3\{[Ln(ReO_4)_2]ReO_4\} \rightarrow Ln_3ReO_8 + 4ReO_7 \\
&(Ln = Ce\text{–}Nd)
\end{aligned}
\qquad (2)
$$

$$3\{[Ln(ReO_4)_2(HMPA)_4]ReO_4\} \rightarrow$$
$$3\{[Ln(ReO_4)_2(HMPA)_{5/3}]ReO_4\} + 7HMPA \rightarrow$$
$$3\{[Ln(ReO_4)_2(HMPA)]_{1/3}ReO_4\} + 4HMPA \rightarrow \quad (3)$$
$$Ln_3ReO_8 + 4Re_2O_7 + HMPA$$
$$(Ln = Sm\text{–}Lu, Y)$$

The data for the final residues are, in general, in good agreement with those expected for the composition Ln_3ReO_8 [2,3]. In the compounds from lanthanum to neodymium a few low values were observed, probably due to the presence of small amounts of the respective oxides resulting from decomposition of Ln_3ReO_8 (compare with data observed by Plyuschev et al. [4–6]).

REFERENCES

1 G. Vicentini, L.B. Zinner and S.M.F. Barreto, An. Acad. Bras. Ciênc., 59 (1987) 341.
2 G. Band and M. Capestan, Bull. Soc. Chim. Fr., 12 (1967) 4685.
3 G. Vicentini, L.B. Zinner and P.O. Dunstan, Thermochim. Acta, 118 (1987) 305.
4 V.E. Plyushchev and M.B. Varfolomeev, Khim. Teknol., 8 (1965) 361; Chem. Abstr., 63 (1965) 15789e.
5 V.E. Plyushchev and M.B. Varfolomeev, Russ. J. Inorg. Chem., 10 (1965) 55.
6 V.E. Plyuschev, V.M. Amosov and M.B. Varfolomeev, Dokl. Akad. Nauk SSSR, 150 (1963) 105; Chem. Abstr., 59 (1963) 6013g.