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Note

THERMOANALYTICAL STUDIES OF Lu_2O_3– AND Yb_2O_3–ALKALI PERSULFATE BINARY SYSTEMS

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Binary mixtures of rare earth oxides–alkali persulfates have been investigated [1–8]. Some of them behaved like semiconductors and drastically catalyzed the thermal decomposition reactions of the persulfates; others did not show signs of catalytic activity but reacted with the persulfates and formed alkali metal double salts, disulfates and trisulfates. It is well known that lutetium and ytterbium have similar electronic configurations, $Z=71$ and 70, respectively, and lutetium has an ionic radius of 1.734 compared with 1.699 for ytterbium; their sesqioxides have little oxidizing power and high melting points. Their alkali double salts and sulfates have similar structures and crystalline shapes [9]. Both lutetium and ytterbium sulfates decompose in one step [10], yielding the corresponding oxides. It was thought worthwhile to investigate the thermoanalytical behavior of the two oxides towards sodium and potassium persulfates at elevated temperatures.

EXPERIMENTAL

All the chemicals used in this work were of analytical grade: Lu_2O_3 and Yb_2O_3 (Fluka AG, 99.99% pure); $Na_2S_2SO_8$ and $K_2S_2O_8$ (Hopkin and Williams); Al_2O_3 (BDH, calcined at 1300°C for 3 h) was used as reference for DTA. The procedure, equipment, and apparatus employed were as described previously [1].

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RESULTS AND DISCUSSION

Lu_2O_3–$Na_2S_2O_8$

Figure 1 indicates no noticeable catalytic effect on the thermal decomposition of persulfates for the molar ratios 1:6, 1:3, and 2:3. For the 1:2 ratio, the initial decomposition temperature, T_i, was lowered by 10°C due to dilution effect. In the case of the 1:1 ratio the T_i assumed 210°C instead of 190°C for the pure persulfate, that is, its decomposition was retarded by the negative catalysis of the oxide. The fusion of the pyrosulfate formed was also catalyzed and its reaction with the oxide eventually occurred at 380–435°C. The largest exotherm of the reaction is observed in the 1:3 ratio (stoichiometric) where about 93.1% of $Na_2S_2O_7$ has already reacted with the oxide.

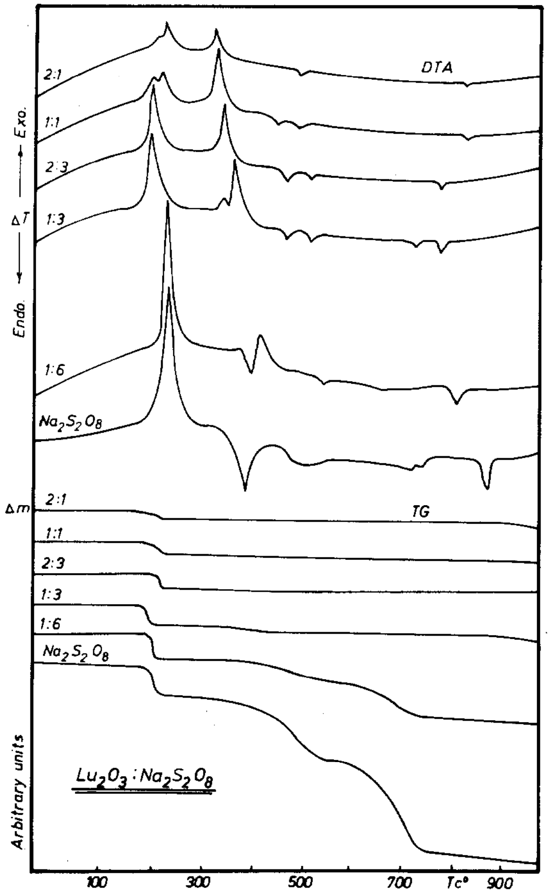

Fig. 1. TG and DTA curves of lutetium(III) oxide–sodium persulfate mixtures.

The XRD patterns of samples heated up to 515, 640, and 1000°C showed the *d*-lines 3.398, 3.530, 5.500 Å. Attempts were made to match these lines with those available within ASTM and JCPDS cards; the search was unsuccessful due to the lack of available data. However, indications of the formation of the double salt, $NaLu(SO_4)_2$, are obtained from the TG curve calculation, and the fact that lutetium(III) is a rare earth metal which should form double salts, $MRE(SO_4)_2$, where M is either Na or K and RE is a rare earth [31]. Consequently the stoichiometric reaction is represented as

$$Lu_2O_3 + 3\ Na_2S_2O_7 \xrightarrow{\Delta} 2\ NaLu(SO_4)_2 + 2\ Na_2SO_4$$

For the molar ratios 1:6 and 2:3, 45 and 92.8%, respectively, react with the oxide.

The two endo-peaks appearing consecutively at 480 and 550°C refer to a crystalline phase transition for the double salt. No evidence can be presented here as to the nature of this transformation, whether β to α or the reverse. They show up clearly at ratios 1:3, 2:3, and 1:1. The small (1:3) melting endotherm of the salt appears at 730–750°C. This is succeeded by the melting endotherm of impure sodium sulfate, a by-product of the reaction.

Lu_2O_3–$K_2S_2O_8$

The thermal curves for the molar ratios 1:6, 1:3, 2:3, 1:2, and 1:1 are given in Fig. 2. For the 1:6 ratio the T_i for the decomposition of the persulfate is lowered by 20°C. A retarding effect equivalent to 10°C was obtained for the 1:2 ratio. This rather mild catalysis is related to the amount of oxide present; small amounts accelerate, whereas large amounts decelerate the decomposition. Other molar ratios did not exhibit catalytic activity.

The big exo-peak appearing at 350–380°C and, particularly for the ratio 1:3, suggests the following stoichiometric reaction

$$Lu_2O_3 + 3\ K_2S_2O_7 \xrightarrow{\Delta} Lu_2(SO_4)_3 + 3\ K_2SO_4$$

X-Ray diffractometric analysis for samples heated to 400°C gave *d*-lines (3.28, 7.36, 2.82 Å) which do not match those available for the double salt $KLu(S)_4)_3$ [11], the oxide, the sulfide or the oxysulfate. Moreover, the double salt is unstable at 480°C. Since it is known that the chemical behavior of lutetium and ytterbium is similar, and since the latter forms ytterbium sulfate which decomposes at 900°C [11], Lu(III) probably forms a similar sulfate, such as $Lu_2(SO_4)_3$ which has also been seen to decompose at 900°C.

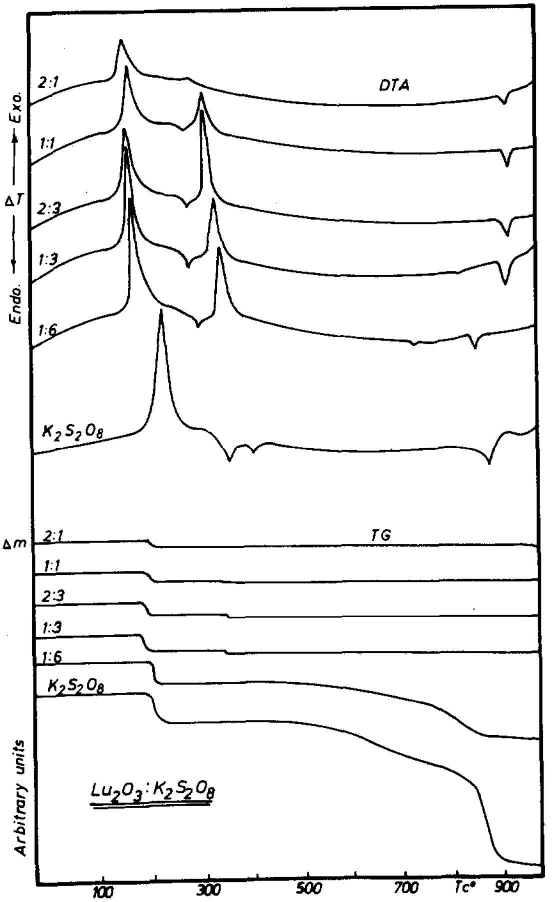

Fig. 2. TG and DTA curves of lutetium(III) oxide–potassium persulfate mixtures.

Yb_2O_3–$Na_2S_2O_7$

Figure 3 exhibits the TG and DTA curves of the various ratios analyzed. Calculation of the TG curves reveals that in the case of the molar ratio 1:3 (stoichiometric) about 80% by weight of the produced pyrosulfate reacts with the oxide at 375–480°C. This is indicated by the small and large exotherms of the stoichiometric reaction

$$Yb_2O_3 + 3\,Na_2S_2O_7 \overset{\Delta}{\rightarrow} Na_2Yb_2(SO_4)_4 + 2\,Na_2SO_4$$

These two consecutive endotherms indicate that this reaction occurs during and after the fusion of $Na_2S_2O_7$. The fusion endotherm (1:3 ratio) of pure sodium persulfate was abolished due to thermal neutrality at 375°C.

Samples for the molar ratio 1:3, heated between 375 and 900°C, exposed

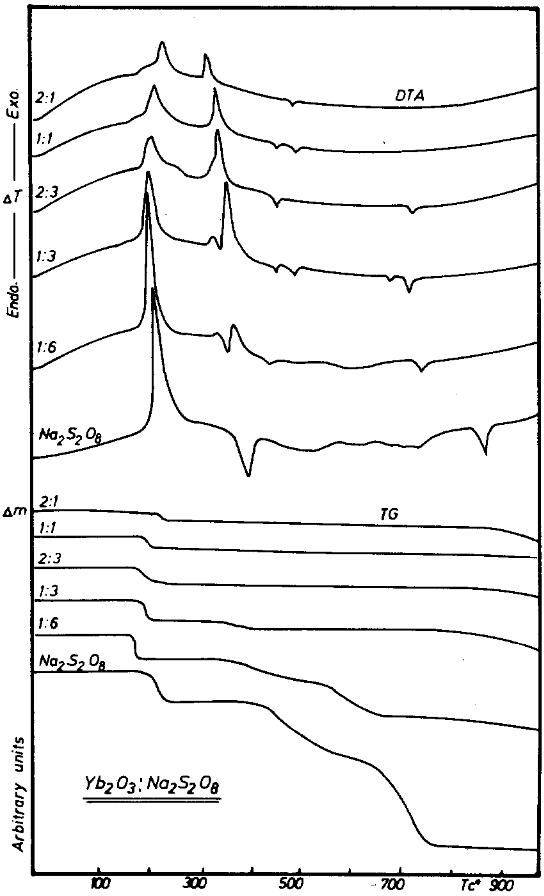

Fig. 3. TG and DTA curves of ytterbium(III) oxide–sodium persulfate mixtures.

XRD patterns (3.398, 3.530, and 5.500 Å) which do not adequately match those belonging to Yb_2O_3 (4.41, 3.03, and 2.48 Å), nor with Yb_2O_3 (3.015, 2.612, and 1.843 Å) [12]; also calculation from TG curves indicates the formation of $Na_2Yb_2(SO_4)_4$. DTA curves and those available in the literature do not coincide [10], excluding the formation of $Yb_2(SO_4)_3$. Other lanthanides, such as Eu_2O_3, Tb_2O_3 and Er_2O_3, react with sodium pyrosulfate at elevated temperatures to form double salts of formula $Na_2RE_2(SO_4)_4$. Finally, the results obtained suggest the latter salt as the final product of the above stoichiometric reaction.

The salt remains thermally stable up to 900°C. Thereafter it decomposes very slowly; for instance at 1050°C no more than 2% was actually degraded. The three endotherms on the DTA curves of the 1:3 molar ratio at 493, 553, and 730°C represent some sort of polymorphic equilibrium. These phases showed no signs of fusion, and were white in color; their XRD patterns were identical.

Yb_2O_3-$K_2S_2O_8$

One of the accentuated features of this system (Fig. 4) is the 1 : 3 stoichiometric molar ratio in which the oxide plays the role of a catalyst by lowering the T_i of the decomposition of $K_2S_2O_8$ into $K_2S_2O_7$ by 15°C. Another feature is that about 90% by weight (optimal) of $K_2S_2O_7$ reacts with the oxide to form ytterbium(III) sulfate at 345°C. Mixtures of the stoichiometric ratio on heating up to 600°C and cooling gave bright lines at 3.287, 7.365, and 2.777 Å. However, these lines matched neither those recognized as

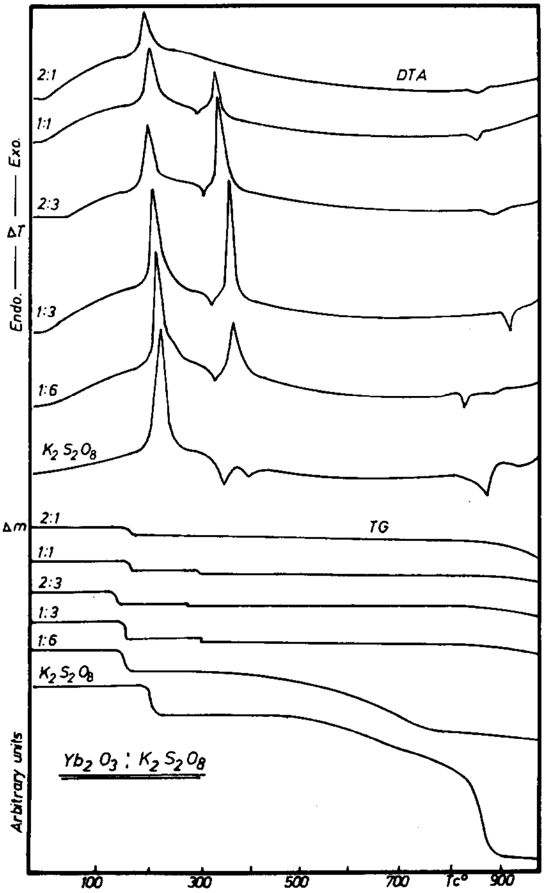

Fig. 4. TG and DTA curves of ytterbium(III) oxide–potassium persulfate mixtures.

$KYb(SO_4)_2$ (3.77, 2.913, 8.473 Å) nor those for $YbSO_4$ [13].

Nevertheless, a close similarity was found between the DTA curves of the compound studied and those in the literature for $Yb_2(SO_4)_3$ [10], in addition to the results of chemical analysis of the decomposition products. Therefore the stoichiometric reaction can be depicted as

$$Yb_2O_3 + 3\,K_2S_2O_7 \xrightarrow{\Delta} Yb_2(SO_4)_3 + 3\,K_2SO_4$$

The sharp exo-peaks of the above reaction appear at all molar ratios except 2:1, where thermoneutrality occurs; their heights are almost proportional to the per cent of $Yb_2(SO_4)_3$ formed, and they reach a maximum at 1:3.

The DTA curves for 1:6, 1:3, 2:3, 1:1, and 2:1 ratios exhibit melting endotherms of different peak areas at 850, 940, 890, 885, 880°C, respectively. The white crystalline ytterbium(III) sulfate decomposes into Yb_2O_3 and SO_3, the presence of which was checked by X-ray diffractometry and chemical analysis.

REFERENCES

1 F. Jasim and K.R. Idan, J. Therm. Anal., 21 (1981) 249.
2 J.R. Igal and F. Jasim, Thermochim. Acta, 54 (1982) 93.
3 J.R. Igal and F. Jasim, Thermochim. Acta, 54 (1982) 263.
4 H.J. Jaffer and F. Jasim, Thermochim. Acta, 45 (1981) 39.
5 H.J. Jaffer and F.Jasim, Thermochim. Acta, 45 (1981) 49.
6 K.I. Hussain and F. Jasim, Thermochim. Acta, 54 (1982) 87.
7 K.I. Hussain and F. Jasim, Thermochim. Acta, 55 (1982) 173.
8 F. Jasim, M.M. Barbooti and K.I. Hussain, Thermochim. Acta, 58 (1982) 289.
9 S. Prakash, Advanced Chemistry of Rare Elements, Chand and Co. Ltd., New Delhi, 1975.
10 M.W. Nathans and W.W. Wendlandt, J. Inorg. Nucl. Chem., 24 (1962) 873.
11 K.Z. Zakieva, P.D. Rabina, I.E. Zubova, A.M. Batanova, Tr. Mosk., Khim. Technol. Inst., 73 (1973) 117; Chem. Abstr., 81 (1974) 96721 g.
12 ASTM Cards 17-774.
13 P.A. Degtiarev, A.N. Pokrovskii, L.M. Kovba and F.M. Korytnaia, J. Solid State Chem., 22 (1977) 419.