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THERMAL AND X-RAY STUDIES OF BINARY RARE EARTH SESQUIOXIDES – ALKALI METAL PERSULFATE SYSTEMS

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Three binary systems, each consisting of mixtures of different molar ratios of a rare earth (4*f* metal) sesquioxide and sodium or potassium persulfate (peroxodisulfate) have been investigated under static (air) atmospheres using a derivatograph. For each system ($R_2O_3 - M_2S_2O_8$, where R is Sm, Gd, or Dy, and M is K or Na), the molar ratios that represent stoichiometric reactions were fixed. Calculations were based on data obtained from T, TG, DTG and DTA curves. Intermediate and final products were mainly identified by X-ray diffractometry. Double salts of Sm, Gd, and Dy were thermally prepared by solid-state reactions. It was found that one such double salt $KDy(SO_4)_2$, forms a eutectic mixture with K_2SO_4 and also that both Gd and Dy sesquioxides behave as *p*-type semiconductors and therefore exhibit catalytic activities towards the thermal decomposition of persulfates and pyrosulfates. Optimal catalysis was obtained with molar ratios of 1 : 3. The activities increased as the ionic radii of these metals decrease: Sm, Gd, Dy.

Several investigators have used TG, DTG and DTA to study the non-isothermal (dynamic) decompositions of pure $Na_2S_2O_8$ and $K_2S_2O_8$ and the decompositions catalyzed by metal oxides such as CuO, TiO_2, Zn [1–5], oxides with a corundum structure such as Al_2O_3, Cr_2O_3 and Fe_2O_3, and oxides with a cubic structure such as CdO [6], to establish their catalytic effects on the decomposition and concluded that these effects increased with the *p*-type semiconductor characters of the catalyst, thereby supporting previous findings [6].

It was found that some of the rare earth sesquioxides act as semiconductors at high temperatures. For instance, both Gd_2O_3 and Dy_2O_3 exhibit *p*-type semiconductor activities at pressures of $10^{-9.4}$ and $10^{-11.3}$ atm and at temperatures of 727–1177° and 727–1377° respectively [8]. Furthermore, it has been shown [7, 9] that Sm_2O_3, Gd_2O_3 and Dy_2O_3 exert catalytic effects by lowering the thermal decomposition temperatures of lithium perchlorate and lithium carbonate.

A thermogravimetric study of the thermal decomposition of formic acid over lanthanide oxides such as Sm_2O_3 and Dy_2O_3 revealed that the decomposition occurs at 300–400° *via* a lanthanide formate intermediate, which transformed to an oxycarbonate and then cracked to liberate CO_2, with reformation of the lanthanide oxide [10].

The present paper deals with the influences of the three sesquioxides on the decompositions of the peroxodisulfates of sodium and potassium and their

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decomposition products, from the viewpoints of catalysis, the preparation of intermediates and final products, and the formation of eutectic mixtures, over a heating programme from ambient to ceiling temperatures (~1050°).

Experimental

Materials

All the chemicals used in this work were of analytical grade: Sm_2O_3, Dy_2O_3 and Gd_2O_3 (Koch–Light, 99.9 per cent pure); α-Al_2O_3 (BDH, calcined at 1300° for 3 h) was the reference substance for DTA; $Na_2S_2O_8$ and $K_2S_2O_8$ (Hopkin and Williams).

Apparatus

Thermal analysis curves (TG, DTG and DTA) were obtained simultaneously with a Paulik–Paulik–Erdey derivatograph, at a heating or cooling rate of 10°/min, in static (air) atmosphere. Platinum crucibles were used as sample and reference (α-Al_2O_3) holders. The crucibles, each containing 200 mg of powdered samples and the inert reference material, were shaken for about 1 minute for regular packing. For the sake of space-saving, the DTG graphs are not included here. To verify the reproducibility of the results obtained from the thermoanalytical curves, two identical curves obtained in several runs were considered and taken as the basis for the required calculations.

X-ray diffractograms (XRD) were recorded using a Philips diffractometer with (CuK_α) X-radiation, a Ni-filter, 40 KV, 20 mA and a scanning speed of 2°/min. The samples for X-ray measurements were heated up to the temperature indicated for preparation of the mixture with the given molar ratio and then cooled at room temperature.

For each binary system $R_2O_3 - M_2S_2O_8$, the calculated molar ratios of the rare earth sesquioxide and persulfate were mixed and finely ground in an agate mortar for 20 min, dried at 80° for 2 h and then stored in stoppered specimen phials till subsequent use.

Results and discussion

The $Sm_2O_3 - Na_2S_2O_8$ system

The TG and DTA curves of different molar ratios of the binary system $Sm_2O_3 - Na_2S_2O_8$ are presented in Fig. 1. Careful comparison of theTG curves of pure $Na_2S_2O_8$ and the mixtures reveals the occurrence of a chemical reaction between the oxide and the thermally formed pyrosulfate over the temperature range

380–410°. After being preheated up to the temperature indicated and cooled to room temperature, on subsequent XRD examination the samples gave data indicating that they were isostructural with the compound $NaSm(SO_4)_2$ [11] (Table 1). However, it is to be noted that this reaction reached a maximum rate of completion at the molar ratio 1 : 3, which was considered as the stoichiometric ratio.

Since the melting point temperature (*T*m) of $Na_2S_2O_7$, represented by the endotherm at 380° (Fig. 1), almost coincides with the exotherm of the stoichiometric reaction, a state of thermal neutrality has been reached; this is a resultant of the overlapping of the melting point endotherm and the reaction exotherm at the indicated temperature. Thermal neutrality was also observed for the molar ratios 2 : 3 and 1 : 1. For the molar ratio 1 : 6 this exothermic reaction took place after the *T*m of $Na_2S_2O_7$. Further on, the solid-phase transition of $NaSm(SO_4)_2$ resulting in the endotherm in the DTA curve at 595° is actually the *T*m of this double sulfate. However, the last endotherm in the DTA curves corresponds to the *T*m of Na_2SO_4 produced as a result of the thermal decomposition of the unreacted $Na_2S_2O_7$, whereas the first sharp endotherm corresponds to the exothermic decomposition [1] of $Na_2S_2O_8$. In fact, this exotherm is due to a secondary process in which O_2 molecules are formed from atomic oxygen.

Table 1

Results of thermoanalytical study of the three binary systems for stoichiometric ratio 1 : 3 $R_2O_3 : M_2S_2O_8$, and of XRD patterns of the double salts produced

Binary systems	Lost O_2, mg		Persulfate Decomp. temp.		Compound formed	Thermal stability	XRD pattern
			T_i,	T_f,			
	Calc.	Found	°C		Formula	°C	d, (Å)
Sm_2O_3– $Na_2S_2O_8$	9.03	12.00	200	250	$NaSm(SO_4)_2$	480–1000	3.46, 2.99, 2.84
Gd_2O_3– $Na_2S_2O_8$	8.80	8.00	200	240	$NaGd(SO_4)_2$	480–1000	3.43, 2.87, 2.84
Dy_2O_3– $Na_2S_2O_8$	8.80	10.00	200	250	$NaDy(SO_4)_2$	480–1000	2.87, 2.79, 2.76
Sm_2O_3– $K_2S_2O_8$	3.56	11.00	180	225	$KSm(SO_4)_2$	620–1000	4.088, 3.309, 1.84
Gd_2O_3– $K_2S_2O_8$	8.16	9.50	180	220	$KGd(SO_4)_2$	600–1000	3.32, 2.84, 2.79
Dy_2O_3– $K_2S_2O_8$	8.08	8.50	190	220	$KDy(SO_4)_2$	420–1000	2.968, 2.92, 2.88

An equation can therefore be set up for the stoichiometric reaction of solid Sm_2O_3 with molten $Na_2S_2O_7$:

$$Sm_2O_3 + 3\,Na_2S_2O_7 \rightarrow 2\,NaSm(SO_4)_2 + 2\,Na_2SO_4$$

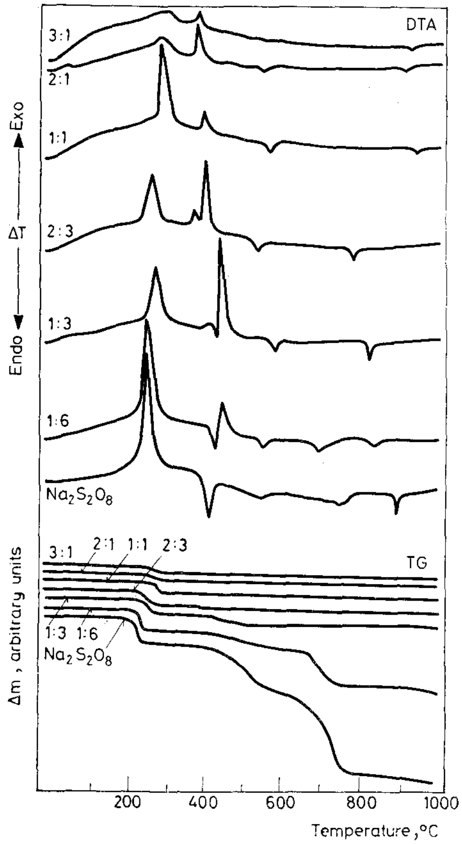

Fig. 1. TG and DTA curves of samarium(III) oxide—sodium persulfate mixture

It has been found that the DTA profiles are influenced by the amounts of the oxide present, as in the case of the molar ratios 2 : 1 and 3 : 1, where the areas under the reaction endotherms decrease; the two small endotherms at 420° in the DTA curves (2 : 1 and 3 : 1) refer to the partial decomposition of the remaining (unreacted) oxide.

The Sm_2O_3 – $K_2S_2O_8$ system

Figure 2 indicates the TG and DTA curves of the mixtures with various molar ratios of the Sm_2O_3 – $K_2S_2O_8$ binary system, as well as those of pure $K_2S_2O_8$. Careful examination of these curves did not disclose any phenomenological catalytic effect of Sm_2O_3 on the initial and final decomposition temperatures of $K_2S_2O_8$. The DTA curve of pure $K_2S_2O_8$ gave two successive endotherms due to the solid-phase [12] transformation β-$K_2S_2O_7 \rightarrow \alpha$-$K_2S_2O_7$. At the molar ratio 1 : 3, cal-

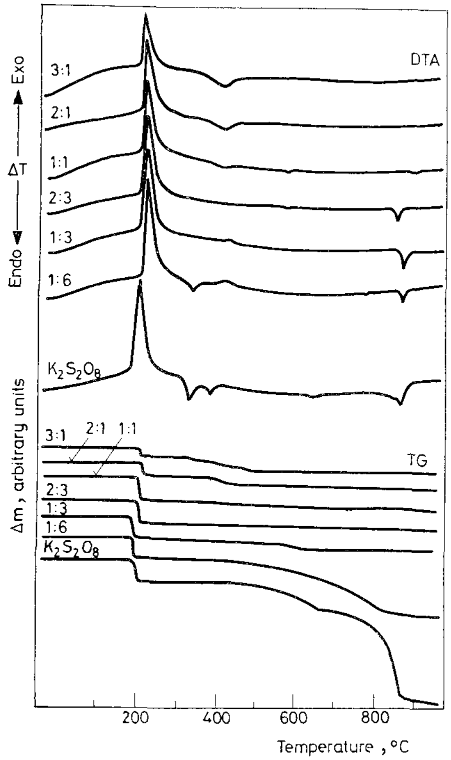

Fig. 2. TG and DTA curves of samarium(III) oxide—potassium persulfate mixtures

culations on the TG curve revealed that about 69 per cent of the thermally produced $K_2S_2O_7$ reacted with the Sm_2O_3 present, and that this reaction occurred in the region of the phase transition of $K_2S_2O_7$ and before its melting: a situation which led to the disappearance of the two endotherms due to the exothermic formation of a new compound whose XRD pattern (Table 1) revealed that it was isostructural with $KSm(SO_4)_2$. This ratio was considered the stoichiometric one, where the reaction goes to completion:

$$Sm_2O_3 + 3\ K_2S_2O_7 \rightarrow 2\ KSm(SO_4)_2 + 2\ K_2SO_4$$

At molar ratios of 1 : 6, 2 : 3 and 1 : 1, the reaction was not stoichiometric. For instance, only 35 per cent of the available $K_2S_2O_7$ reacted with the oxide to form the above compound. It was also found that an increase in the amount of the oxide caused a shift toward a lower initial reaction temperature; this lowering was most probably due to the dilution effect. For example at the molar ratio of 1 : 3 the reaction occurred at ~365°, whilst at 1 : 6 it occurred at ~400°. At molar ratios of 2 : 1 and 3 : 1, blurred or no *d*-lines for the new compound could be identified. This might be caused by the overlapping of the *d*-lines emitted by the unreacted oxide. The sharp endotherms at 840° for the ratios 1 : 6, 1 : 3, 2 : 3 and 1 : 1 represented the melting point of $KSm(SO_4)_2$. It is clear from the TG curves that the compound is thermally stable between 620 and 1000°. This opens up the possibility of using this salt as a supporting medium for other thermal reactions.

The broad endotherm at 420°, which is seen for molar ratios of 3 : 1 and 3 : 2, refers to the slight thermal decomposition of Sm_2O_3 into SmO and O_2.

The Gd_2O_3 – $Na_2S_2O_8$ system

Scrutiny of the DTA and TG curves (Fig. 3) reveals a small exotherm in the DTA curve just before the high exo peak of O_2 formation. In the TG curve it appears as a small notch bisecting the shoulder, showing that the degradation of persulfate to pyrosulfate occurs in two stages, perhaps due to the formation of intermediates as a result of the catalytic activity of the Gd_2O_3, which retards the

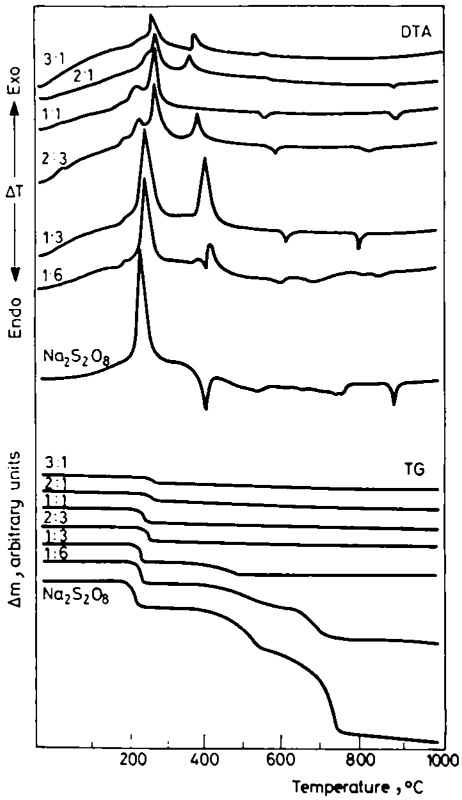

Fig. 3. TG and DTA curves of gadolinium(III) oxide—sodium persulfate mixtures

abrupt decomposition of the persulfate. The existence of this notch is independent of the molar ratio. However, preheated and cooled samples, isolated just before and after the notch, did not yield XRD spectra attributable to any gadolinium persulfate species. This in turn confirms the extraordinary thermal instability of the intermediate, if any.

At a molar ratio of 1 : 3 about 82 per cent (stoichiometric) of the thermally produced pyrosulfate reacted with the Gd_2O_3. This was indicated by the sharp exotherm at 385° (which is simultaneously the melting point temperature of the pyrosulfate). Thereafter, samples preheated between 480 and 1000° gave *d*-spacing data (Table 1) corresponding to a compound isostructural with $NaGd(SO_4)_2$; thus, the following stoichiometric reaction is suggested for its formation:

$$Gd_2O_3 + 3\,Na_2S_2O_7 \rightarrow 2\,NaGd(SO_4)_2 + 2\,Na_2SO_4$$

The 1 : 3 thermoanalytical curves demonstrate that $NaGd(SO_4)_2$ is thermally stable between 480 and 1000°, and that it undergoes a phase transition as indicated by the endotherm at 580°; XRD analysis proved that this endotherm was not related to the melting point temperature of the compound.

Further, thermal neutrality was observed in the 1 : 1 DTA curve where the reaction exotherm eliminated the melting point endotherm of $Na_2S_2O_7$ because of their equal enthalpies.

Naturally, the last sharp endotherm appearing at all molar ratios was the melting point endotherm of the Na_2SO_4 formed.

The Gd_2O_3 – $K_2S_2O_8$ system

The chemical reaction between Gd_2O_3 and $K_2S_2O_8$ was observed in the thermal curves (Fig. 4) by the loss in mass of the sample, beginning around 390°, that is substantially after the *T*m of the thermally produced $K_2S_2O_7$. This finding is best seen for the 1 : 3 molar ratio, where about 85 per cent (stoichiometric) of the pyrosulfate reacts with the Gd_2O_3. This is more clearly indicated by the relative increase in the area of the endo peaks (or enthalpies) of both the β to α phase transition and the melting of pyrosulfate. The TG curve exhibits a broad horizontal plateau between 600 and 1000°. Samples of 1 : 3 oxide to persulfate, preheated within this plateau gave identical diffractograms with characteristic lines, as is evident from Table 1.

However, these *d*-lines were not found to correspond with those available in ASTM or JCPD files. Accordingly, on the basis of chemical analysis and TG analytical computation, $KGd(SO_4)_2$ was proposed as the chemical formula for the compound, formed in the following stoichiometric reaction:

$$Gd_2O_3 + 3\,K_2S_2O_7 \rightarrow 2\,KGd(SO_4)_2 + 2\,K_2SO_4$$

The new compound undergoes a phase change, as recorded by the small endothermic effect in the TG curve at 825°. To make sure that this change was due

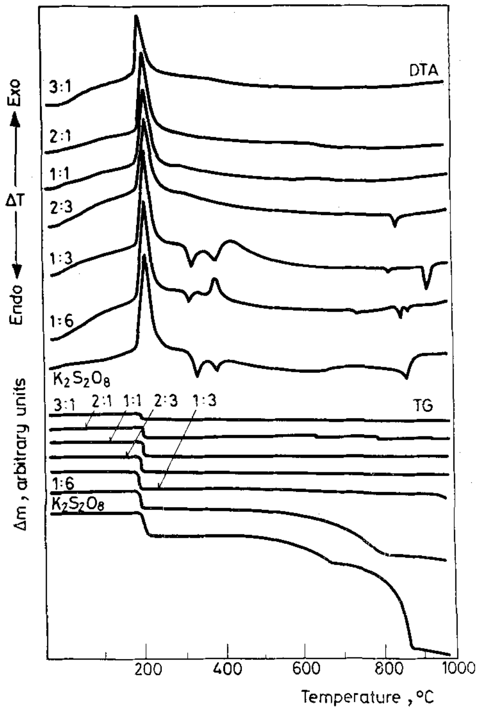

Fig. 4. TG and DTA curves of gadolinium(III) oxide—potassium persulfate mixtures

not to melting, but to a polymorphic transition the XRD patterns for samples preheated at 800 and 880° were studied. They were found to be identical, that is no melting occurred in between these two temperatures and therefore the endotherm confirmed a phase transition only. Also, the DTA for this same ratio showed an irreversible sharp melting endotherm (without mass loss in the TG) in the vicinity of 920°, which is most probably associated with the *T*m of $KGd(SO_4)_2$ in the presence of negligible amounts of K_2SO_4. A compact cake was obtained after cooling the contents of the crucible to ambient conditions. Eventually, the phase change as well as the melting endotherm disappeared at the molar ratios 1 : 1, 2 : 1 and 3 : 1, perhaps due to the formation of trace quantities of compounds which were undetectable by the instrument. On the other hand, they were observed at ratios of 1 : 6 and 2 : 3. It seems, therefore, that the presence of excess oxide retards it. No adequate explanation can so far be offered for this chemical reaction.

The Dy_2O_3 – $Na_2S_2O_8$ system

Figure 5 shows the results of the thermoanalytical investigations of this binary system with Dy_2O_3 – $Na_2S_2O_8$ molar ratios of 1 : 6, 1 : 3, 2 : 3, 1 : 1, 2 : 1 and 3 : 1. At the first three ratios, the dysprosium(III) oxide reacts with the thermally

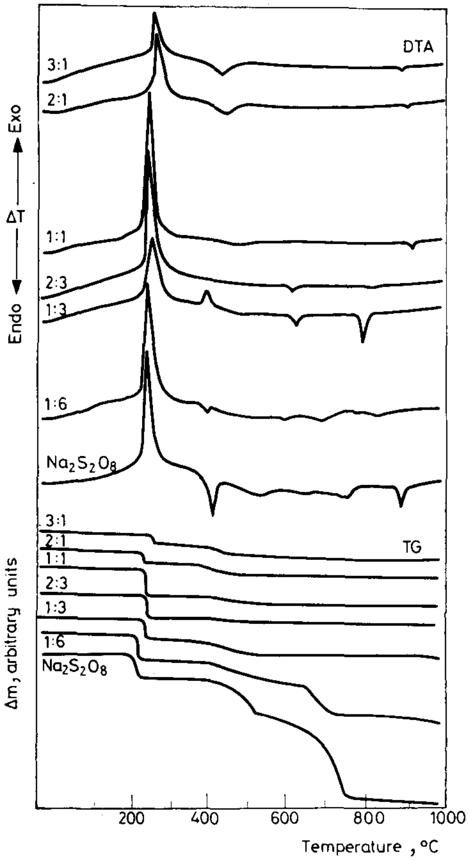

Fig. 5. TG and DTA curves of dysprosium(III) oxide—sodium persulfate mixtures

produced pyrosulfate just after the *T*m of the latter. At other molar ratios, however, the reaction starts before melting of the pyrosulfate. As mentioned and interpreted above, the excess oxide lowers the initial temperature of the reaction system.

Furthermore, the net change in enthalpy of the system is optimal for the 1 : 3 ratio. This can be appreciated both from the height of the short exotherm at 410°, and from the fact that 85 per cent of the available pyrosulfate reacted with the oxide. To identity the compound formed XRD analysis was conducted on samples preheated between 500 and 1000°. Their XRD patterns (Table 1) indicated the presence of $Dy_2(SO_4)_3 \cdot Na_2SO_4 \cdot 2\,H_2O$. Since the presence of water of hydration is impossible at temperatures as high as 1000°, it must be remembered that XRD patterns normally relate to unit cell structure, which need not differ in the absence of water of hydration [13]. Consequently, the detected salt was considered to be anhydrous $Dy_2(SO_4)_3 \cdot Na_2SO_4$, or written as the double salt $NaDy(SO_4)_2$, whose stoichiometric equation of formation is

$$Dy_2O_3 + 3\,Na_2S_2O_7 \rightarrow Dy_2(SO_4)_3 \cdot Na_2SO_4 + 2\,Na_2SO_4$$

At the 1 : 3 stoichiometric molar ratio the compound underwent a phase change at 540°, as seen from the endo peak in the DTA. This change was checked from identical XRD patterns of samples preheated before and after 540°. Further, the last endotherm is that of Na_2SO_4, whose *T*m varies from 765° for the 1 : 3 ratio to 795° for the 1 : 6 ratio, where only 47 per cent of the pyrosulfate reacts with the oxide.

The Dy_2O_3 – $K_2S_2O_8$ system

TG and DTA analysis of experimental data obtained for this binary system with Dy_2O_3 – $K_2S_2O_8$ molar ratios of 1 : 6, 1 : 3, 2 : 3, 1 : 1, 2 : 1 and 3 : 1 (Fig. 6) indicated that 1 : 3 is the stoichiometric ratio for the reactants; this is suggested by the major exotherm (at which the enthalpy change is at a maximum) at 362° in the DTA curve, that is immediately after the β – α phase transition,

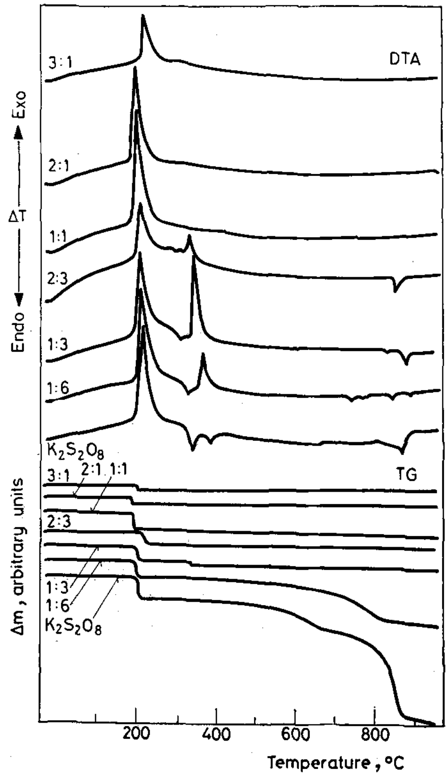

Fig. 6. TG and DTA curves of dysprosium(III) oxide–potassium persulfate mixtures

and before the melting of the pyrosulfate. Calculations from the TG shoulder corresponding to this major exotherm showed that about 92 per cent of the pyrosulfate reacted with the oxide. As a result, samples preheated between 370° and 1000° were carefully scanned with the XRD technique. The XRD patterns (Table 1) point to the formation of $KDy(SO_4)_2$, according to the reaction:

$$Dy_2O_3 + 3\ K_2S_2O_7 \rightarrow 2\ KDy(SO_4)_2 + 2\ K_2SO_4$$

Moreover, the differential thermoanalytical curve of the 1 : 3 mixture (and also the 1 : 6 and 2 : 3 mixtures) showed two endothermal processes. Their diffraction patterns indicated a solid-phase change of the newly detected double salt at 845°, whereas that at 890° proved to be its fusion temperature. It was also observed that a solidified melt formed at the end of the heating programme.

A shift in the size and position of the two endotherms was noticed for the different molar ratios. This shift was apparently caused by variation in the amount of the excess of the thermally stable oxide, in addition to small amounts of K_2SO_4 formed during the reaction.

The disappearance of the two endo peaks at 845° and 890° at the molar ratios 1 : 1, 1 : 2 and 3 : 1 could be ascribed to the amounts of $KDy(SO_4)_2$ formed, which were so small that they lay outside the detection limit of DTA. Actually, the XRD patterns obtained for preheated samples were found to be predominantly those of pure Dy_2O_3.

Comparative studies of the thermal effects of oxides

Effect of ionic radii of Dy, Gd, and Sm

Careful DTA observations at the 1 : 3 molar ratios for the three binary systems (Fig. 7) revealed that, as we pass from $Sm_2O_3 - Gd_2O_3 - Dy_2O_3$, the shapes of the exo peaks of the stoichiometric reactions changed rather drastically. In the presence of Sm_2O_3 the exotherms were much smaller and broader; in the presence of Gd_2O_3 they became sharp and of greater height; whereas in the presence of Dy_2O_3 they were maximum. This behaviour of the sesquioxides was almost the

Table 2

Sequence of ionic radii, activities and thermal stabilities of Dy, Gd, Sm and their double salts

Element	K	Na	Sm	Gd	Dy
At. No.	19	23	62	64	66
Ionic radii	1.53	0.98	1.13	1.11	1.07
Catalysis	—	—	lowest	lower	highest
Therm. stab.	—	—	lowest	lower	highest

same towards both $Na_2S_2O_7$ and $K_2S_2O_7$. The deduction can be made that the exothermicities or changes in enthalpy of the three systems increase with the ionic radii: $Sm^{3+} > Gd^{3+} > Dy^{3+}$. This could be explained by saying that dysprosium with the smallest ionic radius (Table 2) can easily come into contact with the electronegative [7] pyrosulfate ions, forming the double sulfate under conditions of high temperatures and therefore high entropy, which satisfy the collision theory requirements, and so on. Consequently, the process of building up the crystalline structures of the dysprosium double salt is more exothermic than in the cases of the Sm and Gd double salts. This is, of course, equivalent to saying that the thermal stabilities of these salts graduate as: Dy > Gd > Sm. This has been shown to be true by the above experiments. Anyhow, it can be expected with a high degree of probability that the metals with atomic numbers of 65, 63 and 61, under identical conditions, would yield double salts with thermal stabilities intermediate to those of the corresponding double salts of Dy, Gd, and Sm. This prediction will be the subject of future research projects.

Effect of ionic radii of Na and K on positions of exotherms

Figure 7 shows the positions of the exotherms obtained in the reactions of the binary systems of Dy_2O_3 with either sodium or potassium pyrosulfate. It is to be noticed that the exo peak of the 1 : 3 $Dy_2O_3 - Na_2S_2O_8$ system appears after

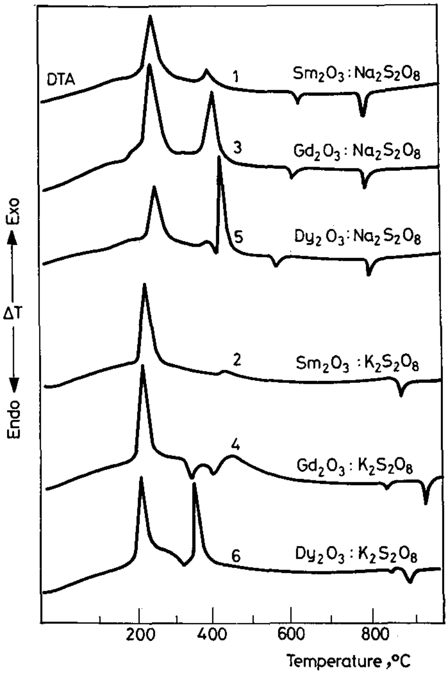

Fig. 7. Comparative effects of the oxides on the reaction exotherms for 1 : 3 ratios

the *Tm* of the pyrosulfate, that is at about 410°, whereas that of the 1 : 3 Dy_2O_3 – – $K_2S_2O_8$ system occurs at around 362°, that is before the *Tm* of $K_2S_2O_7$ but at the beginning of the $\beta - \alpha$ phase change. This shift in exo peak positions by about 50° can be accounted for the ease of interaction of the pyrosulfate of potassium with Dy^{3+}, whose ionic radius differs vastly from that of K^+, and which therefore acts as a strong rival to the latter. Moreover, it seems that the smaller Dy^{3+} ion grasps the opportunity of the $\beta - \alpha$ inversion peak and reacts just before the α-phase formation, where the lattice energy of the unit cell is at a minimum.

On the other hand, in the interaction of Dy^{3+} with the pyrosulfate of sodium, the competition between these two cations is great due to their almost equal ionic radii (Table 2), so that, there should be a high enough temperature for the activation energy of the reacting system to be reached.

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Résumé — Trois systèmes binaires consistant chacun en des mélanges en proportions molaires différentes de sesquioxydes de métaux de terres rares 4 *f* et de persulfate (peroxodisulfate) de sodium et de potassium ont été étudiés en atmosphère statique (air) avec un Derivatograph. Les proportions molaires correspondant aux réactions stoechiométriques ont été fixées pour chaque système ($R_2O_3 : M_2S_2O_8$ où $R =$ Sm, Gd ou Dy et $M =$ K ou Na). Les calculs reposent sur des données obtenues à partir des courbes T, TG, TGD et ATD. L'identification des produits intermédiaires et finaux a été effectuée principalement par diffractométrie des rayons X. Les sels doubles de Sm, Gd et Dy sont préparés par voie thermique, par réactions en phase solide. On a trouvé que l'un de ces sels doubles, $(KDy/SO_4)_2$ forme un mélange eutectique avec K_2SO_4. On a trouvé de même que les deux sesquioxides de Gd et de Dy ont un comportement de semiconducteurs du type *p* et qu'ils montrent une activité catalytique sur la décomposition thermique des persulfates et pyrosulfates. La catalyse optimale est obtenue avec les proportions molaires de (1/3). L'activité augmente quand les rayons ioniques des métaux diminuent: Sm, Gd, Dy.

Zusammenfassung — Drei binäre Systeme, jeweils aus Gemischen verschiedener Molverhältnisse der Sesquioxide der seltenen Erden mit Natrium- oder Kaliumpersulfat (Peroxodisulfat) bestehend, werden in statischer Luft-Atmosphäre unter Einsatz des Derivatographen untersucht. Für jedes System (R_2O_3 : $M_2S_2O_8$, mit R = Sm, Gd oder Dy und M = K oder Na) sind die Molverhältnisse, welche stöchiometrischen Reaktionen entsprechen, festgelegt. Die Berechnungen beruhen auf aus T-, TG-, DTG- und DTA-Kurven erhaltenen Angaben. Die Zwischen- und Endprodukte werden hauptsächlich durch Röntgendiffraktometrie identifiziert. Doppelsalze von Sm, Gd und Dy werden thermisch durch Festphasenreaktionen gebildet. Es wurde gefunden, dass eines dieser Doppelsalze, $KDy(SO_4)_2$, mit K_2SO_4 ein eutektisches Gemisch bildet. Weiterhin zeigte sich, dass sowohl Gd- als auch Dy-Sesquioxide sich wie Halbleiter vom p-Typs verhalten und dadurch gegenüber der thermischen Zersetzung von Persulfaten und Pyrosulfaten katalytische Aktivitäten aufweisen. Die optimale Katalyse wird mit Molverhältnissen von (1 : 3) erzielt. Die Aktivitäten steigen mit abnehmenden Ionenradien der Metalle: Sm, Gd und Dy.

Резюме — С помощью дериватографа исследованы в статической воздушной атмосфере три бинарные системы с различным молярным соотношением полуторных окислов редкоземельных 4f элементов и персульфата натрия или калия. Для каждой системы R_2O_3 : : $M_2S_2O_8$, где R—Sm, Gd, или Dy, а M—K или Na, установлены молярные соотношения, которые соответствуют стехиометрическим реакциям. Расчеты были проведены на основе данных, полученных из Т-, ТГ-, ДТГ- и ДТА-кривых. Промежуточные и конечные продукты реакции идентифицированы в основном с помощью рентгеновской диффрактометрии. Двойные соли Sm, Gd и Dy были получены термически посредством твердотельных реакций. Найдено, что одна из таких солей — $KDy(SO_4)_2$ образует эвтектическую смесь с K_2SO_4. Также установлено, что полуторные окислы Gd и Dy являются полупроводниками p-типа и поэтому проявляют каталитическую активность в реакциях термического разложения персульфатов и пиросульфатов. Оптимальный состав катализаторов получен при 1 : 3 молярном соотношении. Каталитическая активность увеличивается с уменьшением ионных радиусов элементов в ряду: Sm, Gd, Dy.