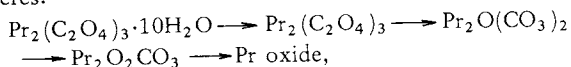


## Thermal Decomposition of Praseodymium Oxalate Hydrate Using a Multiple Technique\*

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The thermal decomposition of praseodymium oxalate decahydrate,  $\text{Pr}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ , was studied in atmospheres of  $\text{He} + \text{O}_2$ ,  $\text{He}$  and  $\text{CO}_2$  by a multiple technique of simultaneous thermogravimetry (TG) and differential thermal analysis (DTA) coupled with evolved gas analysis (EGA). The decomposition proceeded basically by the following steps in all the atmospheres:



yielding  $\text{Pr}_7\text{O}_{12}$  in (4:1)  $\text{He} + \text{O}_2$  mixture, and  $\text{Pr}_2\text{O}_3$  in  $\text{He}$  and in  $\text{CO}_2$  as end products. In  $\text{CO}_2$  atmosphere, the decomposition of anhydrous oxalate took place at higher temperatures than in other atmospheres owing to the stabilization of intermediate carbonates. All the DTA peaks were endothermic in  $\text{He}$  and in  $\text{CO}_2$ , whereas exothermic peaks were also detected in  $\text{He} + \text{O}_2$  probably due to the oxidation of  $\text{CO}$  and deposited carbon, and the disproportionation of  $\text{CO}$ . In inert atmospheres, finely divided carbon particles were markedly deposited, and then reacted with  $\text{CO}_2$  which was evolved during the decomposition of  $\text{Pr}_2\text{O}_2\text{CO}_3$ . Instead of the disproportionation of  $\text{CO}$ , the direct formation of carbon and  $\text{CO}_2$  from  $\text{Pr}_2\text{O}(\text{CO}_3)_2$  was proposed as a possible mechanism for the deposition of carbon particles.

### 1. INTRODUCTION

In recent years, rare earth oxides have been of great interest as potential catalyses, electronic ceramics and refractory materials besides as useful starting materials for the metal production. The thermal decomposition of oxalate is the most widely reported method for the preparation of the oxide. Numerous studies<sup>1-12)</sup> have been carried out on the thermal decomposition of rare earth oxalates, whereas the decomposition mechanism has not been fully established yet, particularly in respect of the intermediate formation. Since physical and chemical properties of the oxide largely depend on its starting material and the

method of preparation, the production route of the oxide is one of the most important factors to determine optimum conditions for providing a product with given properties.

The present authors have made a comparative study on the thermal decomposition of rare earth oxalate taking an interest in the similarity, periodicity and exceptions of chemical and physical natures in rare earth series. Following the previous studies on the oxalates of cerium,<sup>13)</sup> yttrium,<sup>14)</sup> lanthanum<sup>15)</sup> and gadolinium,<sup>16)</sup> the present paper extends to the thermal decomposition of praseodymium oxalate decahydrate mainly employing a multiple thermal analysis technique.

### 2. EXPERIMENTAL

#### 2.1 Preparation of Samples

Praseodymium oxide having a nominal purity of 99.9% was purchased from Rare Metallic Co., Tokyo, Japan. The oxide was dissolved in hot concentrated nitric acid. After dilution of the

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nitrate solution to a concentration of about 0.5 M, insoluble residues were removed by filtration. The oxalate was precipitated at 323 K by dropwise addition of 1 M oxalic acid solution to the vigorously stirred nitrate solution. The precipitate was then filtered after aging at the temperature, thoroughly washed with distilled water and alcohol, and finally air-dried at room temperature. The resulting oxalate corresponded to the apparent formula  $\text{Pr}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$  by ignition to the oxide in air.

In order to characterize decomposition products by X-ray diffraction and infrared absorption spectroscopy, some samples at several stages of decomposition were prepared from the decahydrate by heating in air at a rate of 5 K/min to various temperatures.

### 2.2 Apparatus and Procedures

The thermal decomposition was mostly performed by Rigaku TG-DTA Thermoflex coupled with a laboratory-made EGA equipment having thermal conductivity detectors (TCD). The principle of the apparatus is schematically presented in Fig. 1. Using about 15 mg of sample and  $\alpha\text{-Al}_2\text{O}_3$  as a reference material for DTA, TG-DTA-EGA curves were simultaneously obtained in the atmospheres of  $\text{He}+\text{O}_2$  and He, and TG-DTA curves in  $\text{CO}_2$  atmosphere. Gases were supplied from cylinders with a flow rate of  $60\text{ cm}^3/\text{min}$ . Helium and oxygen were mixed in a ratio of approximately (4:1) by a gas flow rate controller (FRC). In EGA, the mixed gas or helium used as a carrier gas was introduced to the TG-DTA apparatus passing through the reference cells of TCD-1 and TCD-2. All the gases evolved from the sample were transported with the carrier gas to an absorption tube containing  $\text{Mg}(\text{ClO}_4)_2$  in order to eliminate water vapor. Subsequently the gases were flowed to the sample cells of TCD's, and finally released to the atmosphere. A trap packed with Ascarite was

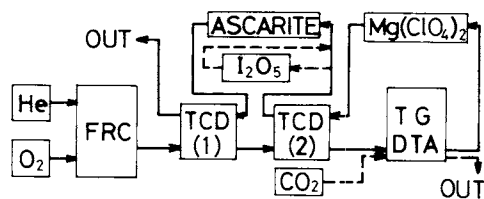


Fig. 1. Schematic arrangement of TG-DTA-EGA apparatus.

properly inserted between the sample cells of TCD-1 and TCD-2 for absorbing  $\text{CO}_2$  liberated. For removing CO in evolved gases, CO was oxidized to  $\text{CO}_2$  by passing through  $\text{I}_2\text{O}_5$  heated at 423 K, and then trapped by Ascarite.

The gas evolution or absorption in the sample was detected by the change in the thermal conductivity of the flowing gas, and was recorded as an unbalanced current of Wheatstone bridge circuit of TCD cells.

Mizutani and Kato<sup>17,18)</sup> have distinguished EGA from a technique called differential thermal gas analysis (DTGA). According to their definition, EGA is a technique of detecting the gases evolved from a sample heated at a controlled rate in an inert carrier gas. In contrary, DTGA is a modified EGA technique in which a sample is heated or cooled at a constant rate in a flow of two or more different mixed gases including an active gas and the changes in the composition of the gas going through a reactor are detected. Based on the definition by ICTA,<sup>19)</sup> EGA is a technique in which the nature and/or amount of volatile products released by a substance is measured as a function of temperature while the substance is subjected to a controlled temperature programme. Therefore, in the present study EGA includes DTGA.

X-ray diffraction patterns were obtained with a diffractometer using Ni-filtered  $\text{CuK}\alpha$  radiation. Infrared absorption spectra were taken by the KBr disk method.

## 3. RESULTS AND DISCUSSION

### 3.1 Thermal Analysis in $\text{He}+\text{O}_2$ Atmosphere

TG, DTA and EGA curves were simultaneously obtained for the thermal decomposition of praseodymium oxalate decahydrate in various conditions. Since water vapor evolved from samples was absorbed by a  $\text{Mg}(\text{ClO}_4)_2$  trap as shown in Fig. 1, no peak was recorded for dehydration in EGA curves of the present study.

Fig. 2 shows the result obtained in a stream of (4:1)  $\text{He}+\text{O}_2$  mixture at a heating rate of 5 K/min. The decahydrate began to release water of hydration at about 310 K accompanying a prominent endothermic peak of DTA. The dehydration occurred rapidly around 390 K, gradually approaching the anhydrous oxalate around 600 K. As in

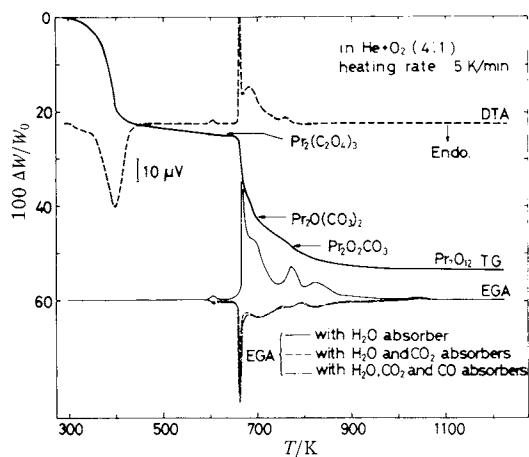


Fig. 2. TG-DTA-EGA curves for the thermal decomposition of  $\text{Pr}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$  in (4:1)  $\text{He} + \text{O}_2$ .

the case of lanthanum oxalate,<sup>15)</sup> it is not obvious that monohydrate is formed as an intermediate during the course of dehydration. Wendlandt et al.<sup>3,4)</sup> and Subba Rao et al.<sup>10)</sup> reported that no intermediate hydrate was detected during the dehydration of  $\text{Pr}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ , whereas Ropp and Gritz<sup>12)</sup> prepared the tetrahydrate depending on the preparation temperature.

The dehydration revealed the same behavior in all the atmospheres employed in the present study.

The TG curve in Fig. 2 exhibited that the decomposition of anhydrous oxalate took place abruptly at about 660 K with a large exothermic peak in the DTA curve, and a gas evolution peak in the EGA curves. A decrease in weight continued gradually to form the oxide as an end product without any definite break or plateau up to approximately 970 K. However, several distinct peaks were observed in DTA and EGA curves, suggesting that the oxalate decomposed through the formation of intermediate carbonates and other possible reactions. The exothermic peaks observed during the decomposition of the oxalate are attributed to the oxidation of CO and C, and the disproportionation of CO.

The composition of the end product in (4:1)  $\text{He} + \text{O}_2$  atmosphere was estimated to be  $\text{Pr}_7\text{O}_{12}$  ( $\text{Pr}_{0.1714}$ ) from other experiments.<sup>20)</sup> The thermal decomposition of praseodymium compounds yields not sesquioxide but nonstoichiometric oxides as a function of temperature and oxygen pressure.

EGA peaks obtained without absorbing  $\text{CO}_2$  corresponded to the evolution of CO and  $\text{CO}_2$  resulted from the decomposition of oxalate. However, the peaks were recognized in the reverse side after  $\text{CO}_2$  was absorbed by an Ascarite trap, suggesting the consumption of oxygen. As described by Mizutani and Kato,<sup>17,18)</sup> CO gas evolved by the thermal decomposition of oxalate reacts immediately with oxygen, which spontaneously leads to a decrease in oxygen content and the formation of  $\text{CO}_2$ , resulting a decrease in thermal conductivity of a carrier gas. After CO was oxidized by  $\text{I}_2\text{O}_5$ , and then absorbed as  $\text{CO}_2$ , EGA gave almost the same curve as that obtained with the singular absorption of  $\text{CO}_2$ . It indicates that CO gas evolved from the oxalate is completely oxidized in the reactor of TG-DTA apparatus.

As it is common in thermal analysis, the peak and onset temperatures of decomposition shifted to higher temperatures with increasing in heating rate.

Although no definite break or plateau was observed at the compositions of intermediate carbonates in the TG curve, the formation of the intermediates was confirmed by X-ray diffraction and infrared spectroscopy on decomposition products of various stages in air. Dioxymonocarbonate  $\text{Pr}_2\text{O}_2\text{CO}_3$  ( $\text{Pr}_2\text{O}_3 \cdot \text{CO}_2$ ) could be identified as type I of tetragonal form or type IA of monoclinic form proposed by Turcotte et al.<sup>21)</sup> Details will be described elsewhere.

### 3.2 Thermal Analysis in He Atmosphere

In order to clarify the formation of intermediate carbonates which was complicated in oxidizing atmospheres, thermal analysis was made in an inert atmosphere. Fig. 3 shows TG-DTA-EGA curves obtained in a stream of He at a heating rate of 5 K/min. The decomposition of anhydrous oxalate started at almost the same temperature and was more sluggish compared with the process in  $\text{He} + \text{O}_2$  atmosphere. Some breaks and plateau-like slopes were recognized in the TG curve, which suggested the formation of intermediates, especially  $\text{Pr}_2\text{O}_2\text{CO}_3$  around 870 K.

After the dehydration process, there existed two endothermic peaks in the DTA curve. A small and prominent one was observed at the initial stage of the oxalate decomposition with the evolution of CO and  $\text{CO}_2$  as it is seen from EGA

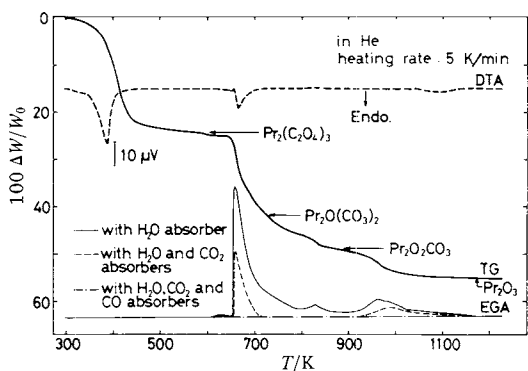
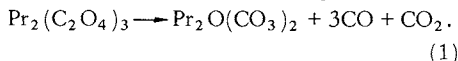


Fig. 3. TG-DTA-EGA curves for the thermal decomposition of  $\text{Pr}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$  in He.

curves. Although the decomposition of the oxalate takes place endothermically, the heat of oxidation of CO to  $\text{CO}_2$  is considered to overcome the heat of decomposition, and thereby the exothermic oxidation of CO masks the endothermic decomposition in oxidizing atmospheres.

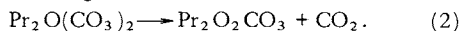
The other small and broad DTA peak was found in the temperature range of 1030 to 1135 K, where no significant change in weight was detected at this stage. Details of this peak will be discussed afterwards.

In EGA curves, the evolution of CO completed once at about 710 K, which corresponded to the composition of monoxycarbonate  $\text{Pr}_2\text{O}(\text{CO}_3)_2$  in the TG curve. Consequently, the first stage of the decomposition of anhydrous oxalate is apparently expressed by the following reaction:



$\text{Pr}_2\text{O}(\text{CO}_3)_2$  is probably unstable and successively undergoes decomposition to give  $\text{Pr}_2\text{O}_2\text{CO}_3$ .

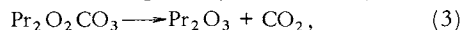
During the decomposition of  $\text{Pr}_2\text{O}(\text{CO}_3)_2$  to  $\text{Pr}_2\text{O}_2\text{CO}_3$ , EGA curves showed the evolution of only  $\text{CO}_2$ , in which a decrease in weight corresponded to the change in the EGA curves. Therefore, this stage is proposed to proceed with the following reaction:



No DTA was detected for this stage presumably due to the slow rate and low heat of reaction.

$\text{Pr}_2\text{O}_2\text{CO}_3$  decomposed to the oxide accompanying the evolution of CO and  $\text{CO}_2$  over the comparatively wide temperature range of 890–1170 K. In an inert atmosphere, the composition

of final oxide is estimated to be  $\text{Pr}_2\text{O}_3$ . If  $\text{Pr}_2\text{O}_2\text{CO}_3$  decomposes by the following reaction:



the evolution of CO gas should not be expected. The formation of dioxycarbonate  $\text{Pr}_2\text{O}_2\text{CO}_2$  which decomposes with the evolution of CO has not been accepted in the decomposition of praseodymium oxalate.<sup>12)</sup>

End products of the decomposition showed a black color, suggesting the deposition of finely divided carbon particles. It has long been proposed that the carbon particles are formed by the disproportionation of primarily evolved CO gas. From the observation of decomposition products at various stages, the deposition of carbon was remarkable during the decomposition of  $\text{Pr}_2\text{O}(\text{CO}_3)_2$ .

It is worth noting that carbon markedly deposits not in the decomposition of  $\text{Pr}_2(\text{C}_2\text{O}_4)_3$  to  $\text{Pr}_2\text{O}(\text{CO}_3)_2$  accompanying the evolution of a large amount of CO, but in the decomposition of  $\text{Pr}_2\text{O}(\text{CO}_3)_2$  to  $\text{Pr}_2\text{O}_2\text{CO}_3$  without any evolution of CO. The disproportionation of CO is an exothermic reaction expressed as



whereas all the DTA peaks are endothermic in He atmosphere. Therefore, the deposition of carbon can not be conclusively explained by the disproportionation of CO, combined with the evolution of  $\text{CO}_2$ . Considering that  $\text{Pr}_2\text{O}(\text{CO}_3)_2$  is unstable and that  $\text{CO}_2$  is thermodynamically more stable than CO at temperatures below about 980 K under the ordinary pressures, such a mechanism could be proposed as carbon and  $\text{CO}_2$  are directly formed by the decomposition of  $\text{Pr}_2\text{O}(\text{CO}_3)_2$ , as discussed in the previous papers.<sup>15,16)</sup>

### 3.3 Thermal Analysis in $\text{CO}_2$ Atmosphere

For the purpose of further examination on the formation of the intermediate carbonates and related reactions, thermal analysis was conducted in  $\text{CO}_2$  atmosphere. Fig. 4 shows TG-DTA curve obtained in a stream of  $\text{CO}_2$  at a heating rate of 5 K/min. The decomposition of anhydrous oxalate took place at higher temperatures than in other atmospheres. The TG curve exhibited more distinct breaks and plateaus in the formation of intermediates, especially at the composition of  $\text{Pr}_2\text{O}_2\text{CO}_3$  which decomposed rapidly at about 1110 K. The final product of decomposition was

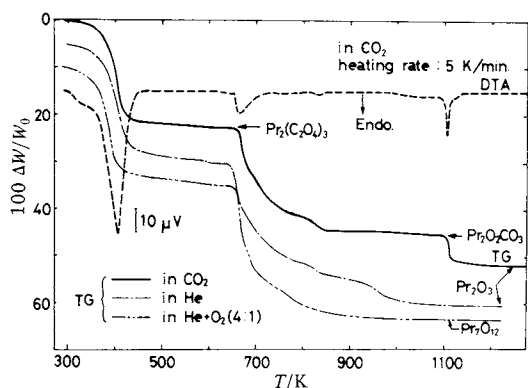


Fig. 4. TG-DTA curves for the thermal decomposition of  $\text{Pr}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$  in  $\text{CO}_2$ .

estimated to be  $\text{Pr}_2\text{O}_3$ .

It has been reported that intermediate carbonates are stabilized in  $\text{CO}_2$  resulting in the decomposition at higher temperatures.<sup>10,12,23</sup> In  $\text{CO}_2$  atmosphere,  $\text{Pr}_2\text{O}_2\text{CO}_3$  is stable at 1088 K by Preiss and Rainer,<sup>22</sup> at 748–1098 K by Subba Rao et al.,<sup>10</sup> and up to 1108 K by Ropp and Gritz.<sup>12</sup> However, Sastry et al.<sup>23</sup> have shown that  $\text{Pr}_2\text{O}_3 \cdot \text{CO}_2$  formed from  $\text{Pr}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$  decomposes at 853 K in  $\text{CO}_2$ . Somiya and Hirano<sup>1</sup> have indicated that the decomposition of praseodymium oxalate hydrate in  $\text{CO}_2$  is described by the sequence:  $\text{Pr}_2(\text{C}_2\text{O}_4)_3 \cdot n\text{H}_2\text{O} \rightarrow \text{Pr}_2(\text{C}_2\text{O}_4)_3 \rightarrow [\text{Pr}_2(\text{C}_2\text{O}_3)_3] \rightarrow [\text{Pr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}] \rightarrow \text{Pr}_2\text{O}_3 \cdot \text{CO}_2 \rightarrow \text{Pr}_2\text{O}_3$ .

In the present study, thermal analysis in stagnant air showed a small but distinct endothermic peak in the DTA curve and a rapid decrease in weight in the TG curve centered at 855 K, where  $\text{Pr}_2\text{O}_2\text{CO}_3$  decomposed to the oxide. It is interpreted as the stabilization of  $\text{Pr}_2\text{O}_2\text{CO}_3$  affected by the self-generated atmosphere of  $\text{CO}_2$ .

Following the main peak for the decomposition of anhydrous oxalate, three endothermic peaks were observed in the DTA curve. An extremely small peak around 830 K corresponded to the decomposition of  $\text{Pr}_2\text{O}(\text{CO}_3)_2$  to  $\text{Pr}_2\text{O}_2\text{CO}_3$ . A small and broad peak was seen over the wide temperature range of 970 to 1140 K. This peak appeared without any significant weight change as it is recognized in He atmosphere. A sharp peak centered at 1110 K was partly overlapped with the broad peak and assigned well to the decomposition of  $\text{Pr}_2\text{O}_2\text{CO}_3$  to the oxide.

In order to prove the broad DTA peaks associated with the decomposition of  $\text{Pr}_2\text{O}_2\text{CO}_3$  in He and in  $\text{CO}_2$ , two kinds of products were prepared by heating the decahydrate to 873 K (sample A) and 1223 K (sample B) at a rate of 5 K/min in He. According to the TG curve in He (Fig. 3), sample A should be composed of mainly  $\text{Pr}_2\text{O}_2\text{CO}_3$ , and sample B  $\text{Pr}_2\text{O}_3$  both with a surplus of carbon. These two samples were examined by DTA in  $\text{CO}_2$  at a heating rate of 20 K/min. The results are shown in Fig. 5. Small and broad peaks covered the wide range of 1100–1180 K in both samples. In sample A, a sharp peak appeared around 1135 K partly overlapping with the broad peak. This peak is attributed to the decomposition of  $\text{Pr}_2\text{O}_2\text{CO}_3$  just as in Fig. 4, although the peak temperature is slightly higher because of the higher heating rate. As a result, the small and broad peak is obviously due to the endothermic reaction expressed as follows:



in which carbon is formed during the decomposition of  $\text{Pr}_2(\text{C}_2\text{O}_4)_3$  or  $\text{Pr}_2\text{O}(\text{CO}_3)$  as before-mentioned. Referring to the DTA curve in He again, the small and broad peak between 1030 and 1135 K can be explained by the reaction of deposited carbon particles with  $\text{CO}_2$  evolved from  $\text{Pr}_2\text{O}_2\text{CO}_3$ . Absence of the endothermic peak for the decomposition of  $\text{Pr}_2\text{O}_2\text{CO}_3$  is probably due to the slow reaction.

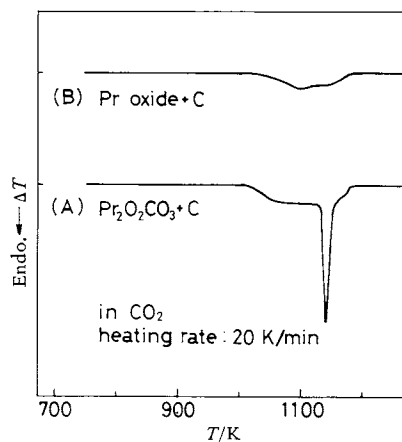


Fig. 5. DTA curves in  $\text{CO}_2$  for the decomposition products obtained by heating  $\text{Pr}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$  in He at a rate of 5 K/min up to 873 K (sample A) and 1223 K (sample B).

In He+O<sub>2</sub> atmosphere, the endothermic peaks for the decomposition of intermediate carbonates may be masked by the exothermic reactions such as the oxidation of CO and carbon, and the disproportionation of CO.

#### 4. CONCLUSION

The thermal decomposition of praseodymium oxalate decahydrate, Pr<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·10H<sub>2</sub>O, was studied by a multiple technique of simultaneous TG-DTA coupled with EGA. The decomposition proceeded basically by the sequence: Pr<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·10H<sub>2</sub>O → Pr<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> → Pr<sub>2</sub>O(CO<sub>3</sub>)<sub>2</sub> → Pr<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> → Pr oxide. In CO<sub>2</sub> atmosphere, the decomposition of anhydrous oxalate took place at higher temperatures than in other atmospheres owing to the stabilization of intermediate carbonates. All the DTA peaks were endothermic in He and in CO<sub>2</sub>, whereas exothermic peaks were also detected in He+O<sub>2</sub>. In inert atmospheres, carbon particles were markedly deposited, and then reacted with CO<sub>2</sub> which was evolved during the decomposition of Pr<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>. Instead of the disproportionation of CO, the direct formation of carbon and CO<sub>2</sub> from Pr<sub>2</sub>O(CO<sub>3</sub>)<sub>2</sub> was proposed as a possible mechanism for the deposition of carbon particles.

#### REFERENCES

- 1) T. Somiya, S. Hirano, *Kogyo Kagaku Zasshi* **34**, 459 (1931)
- 2) T. Duval, C. Duval, *Anal. Chim. Acta* **2**, 218 (1948)
- 3) W. W. Wendlandt, *Anal. Chem.* **30**, 58 (1958)
- 4) W. W. Wendlandt, T. D. George, G. R. Horton, *J. Inorg. Nucl. Chem.* **17**, 273 (1961)
- 5) A. Glasner, M. Steinberg, *J. Inorg. Nucl. Chem.* **16**, 279 (1961)
- 6) A. Glasner, M. Steinberg, *J. Inorg. Nucl. Chem.* **22**, 39 (1961)
- 7) A. Glasner, M. Steinberg, *J. Inorg. Nucl. Chem.* **22**, 156 (1961)
- 8) A. Glasner, E. Levy, M. Steinberg, *J. Inorg. Nucl. Chem.* **25**, 1119 (1963)
- 9) V. V. Subba Rao, R. V. G. Rao, A. B. Biswas, *J. Am. Ceram. Soc.* **47**, 356 (1964)
- 10) V. V. Subba Rao, R. V. G. Rao, A. B. Biswas, *J. Inorg. Nucl. Chem.* **27**, 2525 (1965)
- 11) V. V. Subba Rao, R. V. G. Rao, A. B. Biswas, *J. Inorg. Nucl. Chem.* **28**, 415 (1966)
- 12) R. C. Ropp, E. E. Gritz, "Rare Earth Research" II, ed. L. Eyring, Gordon and Breach, New York (1965), pp. 719-744
- 13) Y. Saito, Y. Shinata, K. Tsuchida, *Funtai Oyobi Funmatsuyakin* **17**, 243 (1971)
- 14) Y. Saito, Y. Shinata, K. Yokota, S. Ikawa, *Funtai Oyobi Funmatsuyakin* **18**, 1 (1971)
- 15) Y. Saito, Y. Shinata, K. Yokota, K. Miura, *Nippon Kinzoku Gakkaishi* **38**, 997 (1974)
- 16) H. Kaneko, Y. Saito, M. Umeda, K. Nagai, *Nippon Kagaku Kaishi* **1977**, 792
- 17) N. Mizutani, A. Kitazawa, M. Kato, *Nippon Kagaku Kaishi* **1972**, 81
- 18) N. Mizutani, M. Kato, *Anal. Chem.* **47**, 1839 (1975)
- 19) G. Lombardi, "For Better Thermal Analysis", International Confederation for Thermal Analysis, Rome (1977)
- 20) Y. Saito, S. Sasaki, T. Maruyama, To be published in the Proceedings of 6th International Conference on Thermal Analysis held at Bayreuth (1980)
- 21) R. P. Turcotte, J. O. Sawyer, L. Eyring, *Inorg. Chem.* **8**, 238 (1969)
- 22) J. Preiss, N. Rainer, *Z. Anorg. Allg. Chem.* **131**, 287 (1923)
- 23) R. L. N. Sastry, S. R. Yoganarasimhan, P. N. Mehrotra, C. N. R. Rao, *J. Inorg. Nucl. Chem.* **28**, 1165 (1966)