

# Thermal decomposition of a mixture of barium and titanyl oxalates

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## Abstract

Thermal decomposition of titanyl oxalate, barium oxalate and a mixture of these two has been carried out, using various thermoanalytical methods, to verify the scheme of thermal decomposition of barium titanyl oxalate proposed by us earlier.<sup>1</sup> Dehydration of titanyl oxalate takes place in two steps, followed by the decomposition of the oxalate to anatase, without involving a carbonate formation. The decomposition of the mixture does not result in the formation of BaTiO<sub>3</sub> below 1000° C. This rules out the possibility of the intermediate formation of BaCO<sub>3</sub> and TiO<sub>2</sub> during the decomposition of barium titanyl oxalate.

Key words : Thermal decomposition, titanyl oxalate, barium oxalate.

## 1. Introduction

This study has been undertaken to compare the mode of decomposition of barium titanyl oxalate reported by us recently,<sup>1</sup> with that of a mixture of barium and titanyl oxalates. It became necessary in view of the points raised by van de Velde and Oranje,<sup>2</sup> particularly that their absorption band of the intermediate compound around 2350 cm<sup>-1</sup> is due to the carbonate group rather than that of entrapped CO<sub>2</sub>. Further, the study is aimed at clarifying the following points: (i) Possible formation of titanyl carbonate as an intermediate during the decomposition of titanyl oxalate; formation of a non-stoichiometric titanyl carbonate has been reported during the decomposition of ammonium and pyridinium titanyl oxalates by van de Velde and Oranje.<sup>2</sup> (ii) Possibility of a solid state reaction below 1000° C, between nascently produced titanium dioxide and barium carbonate. Such a solid state reaction has been postulated by Gallagher and Thomson.<sup>3</sup> (iii) Previous report on the thermal decomposition of titanyl oxalate by Broadbent *et al*<sup>4</sup> is a little confusing.

## 2. Experimental

A number of methods are available in literature for the preparation of titanyl oxalate.<sup>4-6</sup> The ratio of the reagents, their concentration as also the nature of the precipitating medium have considerable effect on the stoichiometry of the precipitated oxalate. Titania gel, free of adsorbed ions, is prepared by hydrolyzing high purity titanium tetra-

chloride (Riedel de Haan). This is dissolved in aqueous oxalic acid, the ratio of  $\text{Ti}:\text{C}_2\text{O}_4$  being maintained at 1 : 2. The resulting clear solution is evaporated at room temperature till oxalic acid just starts to crystallise. Titanyl oxalate is precipitated by adding excess acetone, filtered, washed with acetone and air dried. Analytical results are:  $\text{TiO} = 30.57$ ,  $\text{C}_2\text{O}_4 = 40.67$  and  $\text{H}_2\text{O} = 28.76$  per cent; calculated for  $\text{TiOC}_2\text{O}_4 \cdot 3.5 \text{H}_2\text{O}$ :  $\text{TiO} = 29.74$ ,  $\text{C}_2\text{O}_4 = 40.96$  and  $\text{H}_2\text{O} = 29.32$  per cent.

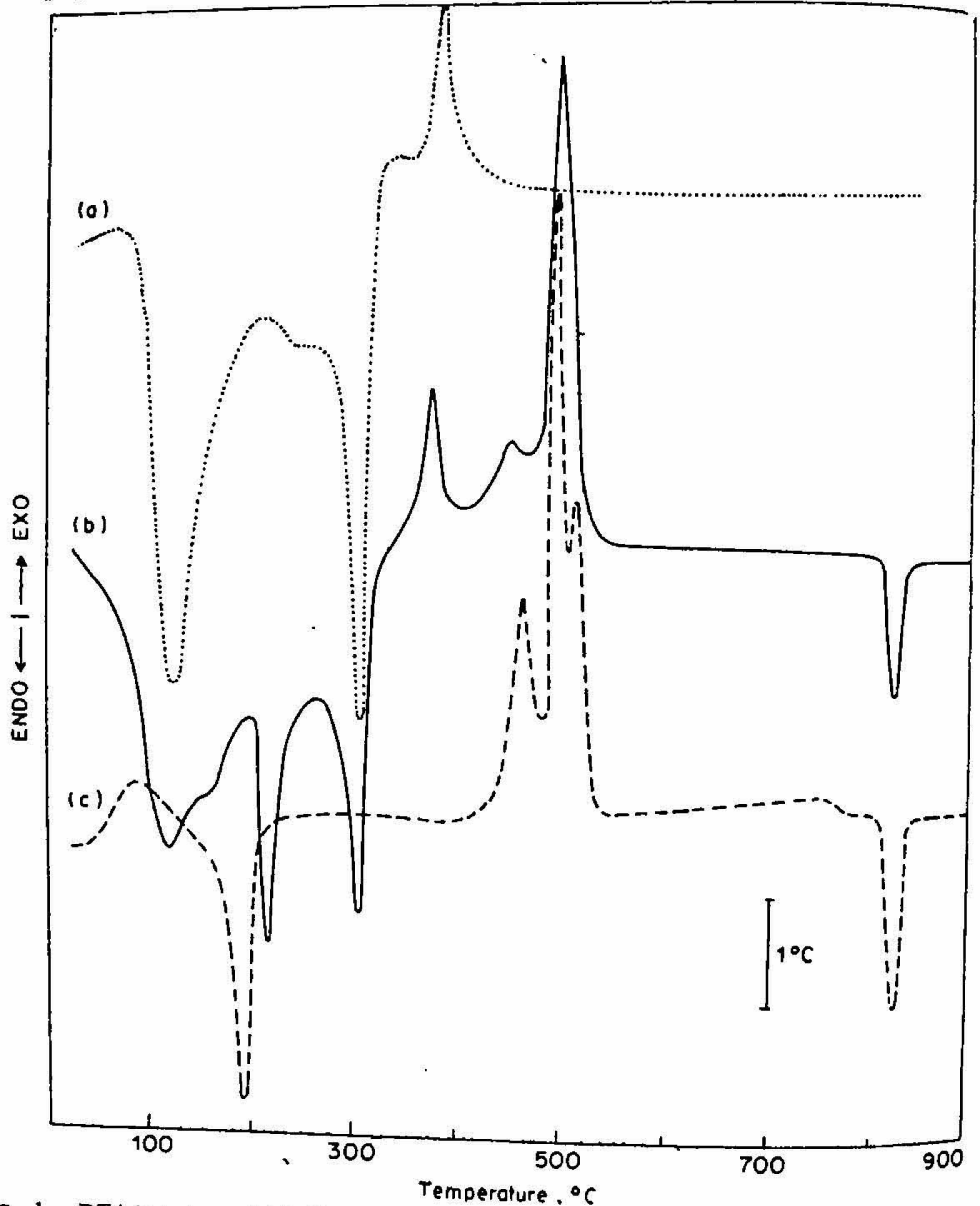


FIG. 1. DTA in oxygen of (a) Titanyl oxalate, (b) mixture of oxalates and (c) barium oxalate.



Barium oxalate is prepared by adding hot aqueous barium chloride to boiling ammonium oxalate solution. The composition of the product formed corresponds to  $\text{BaC}_2\text{O}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$ .

The two oxalates are mixed in 1 : 1 mole proportion in an agate mortar for an hour, using acetone as the medium.

The apparatus for thermal analyses and physico-chemical techniques are described elsewhere.<sup>1</sup>

### 3. Results and discussions

The DTA and TGA are given in Figs. 1 and 2. The DTA of titanyl oxalate in a flowing oxygen atmosphere (Fig. 1 *a*) has the following features : two moles of water are lost in the temperature range of 25 to 160° C (mass loss is 17.4 per cent ; expected 17.76 per cent), while the remaining water is lost between 160 and 260° C. The last dehydration step overlaps with the oxalate decomposition. The latter takes place in a single step and the total mass loss is in excellent agreement with the expected value. There is no indication of the formation of an intermediate carbonate as observed by van de Velde and Oranje<sup>2</sup> during the thermal decomposition of ammonium titanyl oxalate even when the decomposition is carried out in carbon dioxide atmosphere. The oxalate decomposition is endothermic even in oxygen. This is because, the water vapour evolved during the previous dehydration step displaces oxygen in the immediate surroundings of the solid so that further decomposition of oxalate takes place in an apparent atmosphere of water vapour. This prevents the exothermic oxidation of carbon monoxide. The validity of this explanation is further verified by taking isothermally dehydrated titanyl oxalate as the starting material for DTA experiments, whereby exothermic peak is observed in  $\text{O}_2$ . However, the isothermal dehydration of  $\text{TiOC}_2\text{O}_4 \cdot 3.5 \text{H}_2\text{O}$  at 200° C for 24 hours partly loses the oxalate group due to the overlapping of dehydration and decomposition stages. Similar observations for the decomposition of hydrated oxalates are available in literature.<sup>7-9</sup> The exothermic peak following the oxalate decomposition (unaccompanied by any mass loss) is due to the crystallisation of amorphous titanium dioxide to anatase. This has been verified by X-ray powder diffraction data of the residues before and after the exotherm. In isothermal heating experiments, titanyl oxalate decomposes completely at 250° C in two days, forming anatase. At 750° C, the residue is rutile. The endotherm corresponding to the anatase → rutile transformation is not observed in DTA probably due to the low enthalpy of the transformation.

There is no exothermic peak around 500° C in the DTA of titanyl oxalate as reported by Broadbent *et al.*<sup>4</sup> Since these authors prepare titanyl oxalate starting from a fused mixture of potassium hydroxide and titanium dioxide, there is every possibility of potassium oxalate and/or potassium titanyl oxalate being present as impurities in their preparations. Both these oxalates give similar peaks in the same temperature range.<sup>10</sup>

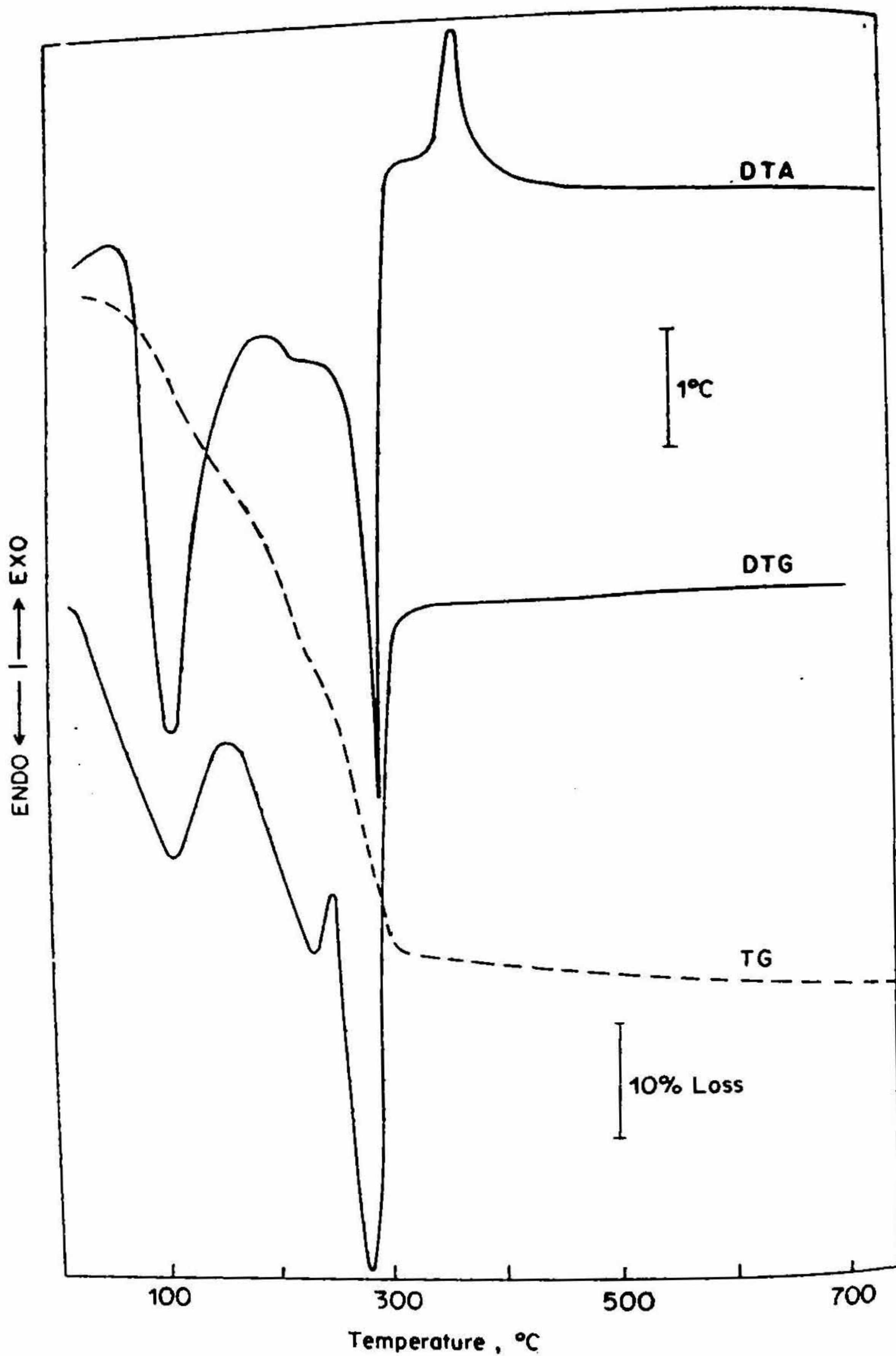


FIG. 2. Thermograms of titanyl oxalate in oxygen.



The DTA of barium oxalate hemihydrate (Fig. 1 c) is in agreement with the earlier reports.<sup>11</sup> It consists of the endothermic dehydration, exothermic decomposition of the oxalate to form barium carbonate and a final endotherm around 815° C due to the orthorhombic → hexagonal reversible transformation of barium carbonate. The triplet nature of the exotherms around 450–520° C is due to (i) the nonequivalent coordination of oxalate groups in the anhydrous barium oxalate and (ii) the oxidation of carbon produced through the disproportionation of carbon monoxide. The attempts to isolate a mixed oxalatocarbonate of barium by isothermal decomposition in the above temperature range always yielded a residue of variable  $C_2O_4/CO_3$  ratio.

The thermogram of the mixture of barium and titanyl oxalates (Fig. 1 b) consists of all the peaks attributable to the individual oxalates at nearly the same temperatures. The only difference noticed is that the peak due to dehydration of barium oxalate is shifted to higher temperature (by about 30° C). This is due to the larger vapour pressure of water formed from the earlier dehydration of titanyl oxalate. The persistence of the peak, corresponding to the phase transformation of barium carbonate at 815° C evidently shows that the solid–solid reaction between barium carbonate and titanium dioxide does not take place even when they are formed in the nascent, reactive state. The X-ray pattern of the residue at 950° C corresponds to a mixture of orthorhombic barium carbonate and rutile. Further, the ir spectrum of the residue obtained just after the oxalate decomposition does not show a peak around 2350  $cm^{-1}$ . This absorption band is observed for the intermediate carbonate formed during the decomposition of barium titanyl oxalate which has been explained as due to the asymmetric stretching band of  $CO_2$  entrapped in the fine-grained solid matrix.<sup>1</sup> This ir band is very weak in the case of the residue from strontium titanyl oxalate and absent for that from calcium titanyl oxalate.<sup>12</sup> The point raised by van de Velde and Oranje<sup>2</sup> that the ir band around 2350  $cm^{-1}$  is due to the overtone of the carbonate frequencies does not seem to be valid since this band is completely absent in the residue of a mixture of titanyl oxalate and barium oxalate heated isothermally at 550° C. Thus it is clear that the thermal decomposition of barium titanyl oxalate does not resemble, at any stage, the decomposition of barium and titanyl oxalates. This study also supports our view that the intermediate residue of composition  $BaTiO_2CO_3$  is not a mixture of reactive  $BaCO_3$  and  $TiO_2$ , as proposed by Gallagher and Thomson.<sup>3</sup>

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