THERMAL ANALYSIS OF SOME METAL ALKOXIDES *

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ABSTRACT

The thermal decomposition of $Al(OPr^i)_3$, $Ca(OEt)_2$ and $Mg(OEt)_2$ has been studied using differential thermal analysis and thermogravimetric techniques. The decomposition products have been isolated and identified by gas chromatography and mass spectrometry. Probable routes for the thermal decomposition of these alkoxides have been proposed

INTRODUCTION

Metal oxides obtained from the thermal decomposition of alkoxides are of submicron particle size and are useful for the preparation of ceramic materials at low temperatures. However, there has been relatively little in-depth study of the thermal decomposition behaviour of the metal alkoxides.
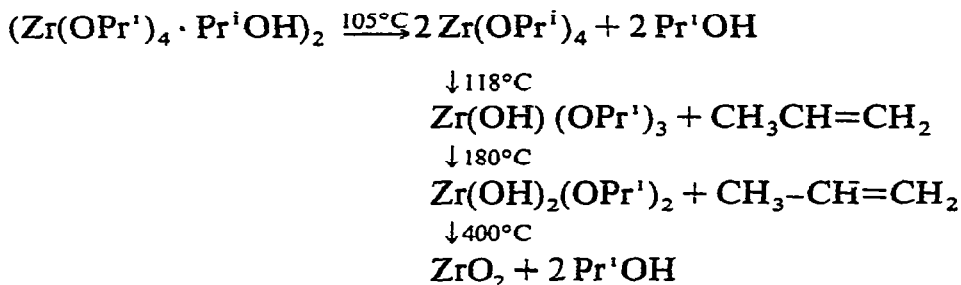
Bradley and Factor [1,2] studied the thermal stability of zirconium isopropoxide at various temperatures and pressures. The products released were identified as propylene, isopropanol, and a solid residue with Zr content intermediate between $Zr_2O_3(OPr^i)_2$ and ZrO_2.

Mazdiyasni et al. [3] studied the pyrolysis of zirconium alkoxides by thermogravimetric analysis. For the tertiary butoxide they proposed a four-step mechanism in which one molecule of olefin and one of alcohol was eliminated alternately. On the other hand, they proposed a two-step mechanism for the decomposition of zirconium isopropoxide. Garson et al. [4] have studied the thermal decomposition of aluminium alkoxides and proposed that the alkoxide decomposes to aluminium oxide, water and olefin.

During the course of our work on the preparation of active metal oxides for solid state studies, we have investigated the decomposition of some metal alkoxides. The results on zirconium isopropoxide have been published [5].

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The following four-step mechanism has been proposed.

$$(Zr(OPr^i)_4 \cdot Pr^iOH)_2 \xrightarrow{105°C} 2\,Zr(OPr^i)_4 + 2\,Pr^iOH$$

$$\downarrow 118°C$$
$$Zr(OH)(OPr^i)_3 + CH_3CH=CH_2$$
$$\downarrow 180°C$$
$$Zr(OH)_2(OPr^i)_2 + CH_3-CH=CH_2$$
$$\downarrow 400°C$$
$$ZrO_2 + 2\,Pr^iOH$$

This mechanism differs from the two-step decomposition given by Mazdiyasni et al. [3] as the derivatogram of zirconium isopropoxide shows three steps in differential thermogravimetry. The present paper is a continuation of this work on the thermal decomposition of alkoxides, and reports the DTA, TG and DTG results of $Al(OPr^i)_3$, $Ca(OEt)_2$ and $Mg(OEt)_2$.

EXPERIMENTAL

Aluminium isopropoxide was prepared from isopropyl alcohol and aluminium metal (foil) by the method of Vogel [6]. Calcium ethoxide was prepared using calcium metal and dry ethanol. Magnesium ethoxide was prepared using magnesium turnings and ethyl alcohol with iodine as a catalyst. The alkoxides were characterized by elemental analysis and IR spectra.

Thermal analysis was carried out in an atmosphere of dry nitrogen using a Paulik and Erdy (MoM Budapest OD-102) derivatograph. A sample of the metal alkoxide (200 mg) was heated in a platinium crucible at a rate of 4°C min^{-1}. Finely powdered alumina was used as reference material. For the analysis of the decomposition products an all-glass apparatus with interchangeable joints was used throughout this investigation (Fig. 1). The compound was placed in a glass flask in an atmosphere of dry nitrogen and heated to the required temperature (below 200°C) in an oil bath. The evolved vapours were condensed in a trap cooled to 0°C and the gaseous decomposition products were condensed in another trap cooled in liquid nitrogen. The compound was then heated at higher temperatures using electrical heating and the evolved liquid and gaseous products were collected in cold traps.

The liquid products were analyzed by gas chromatography. A 20 ft. stainless steel column packed with SE-30 (10%) chromosorb was used. The oven temperature was 60°C and the carrier gas was hydrogen at a pressure of 10 lb in.$^{-2}$ with a flow rate of 50 ml min^{-1}. Gas and liquid products were also identified by mass spectrometry using a CRC 21:110 B Mass Spectrometer.
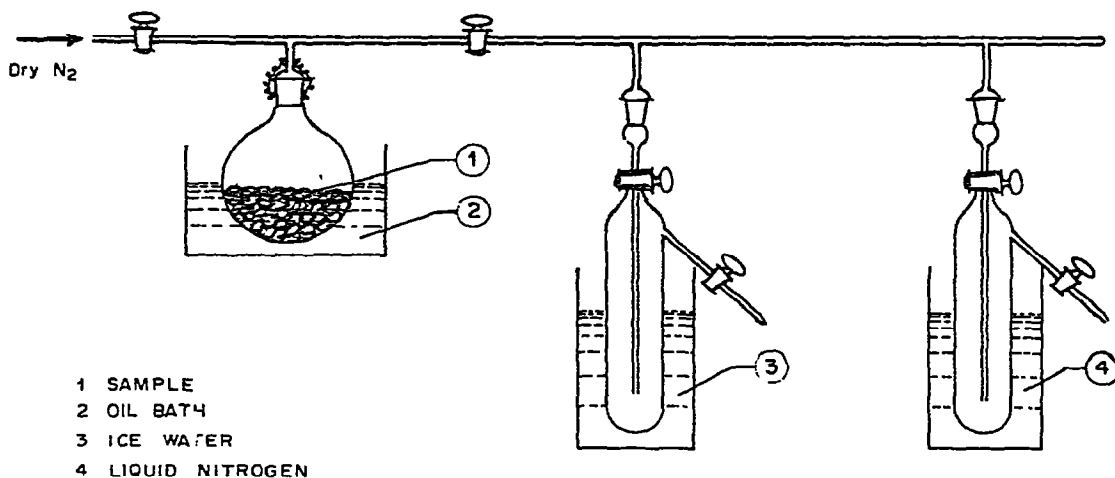
Fig. 1. Apparatus for the analysis of gaseous and liquid products obtained from the thermal decomposition of alkoxides. 1, Sample; 2. oil bath; 3, ice water, 4, liquid nitrogen

RESULTS AND DISCUSSION

Aluminium isopropoxide

The derivatogram of aluminium isopropoxide is given in Fig. 2. The derived data are listed in Table 1. The liquid and gaseous products evolved during a separate decomposition run in the glass unit were identified by gas chromatography and mass spectrometry and the results are given in Table 2.

Mehrotra [7] found that the straight chain aluminium alkoxide was a tetramer $Al_4(OR)_{12}$, whereas the freshly distilled isopropoxide was a trimer, which slowly transformed to a tetramer. In order to explain the aging phenomenon, Bradley [8] suggested a unique structure for its tetramer with a central octahedral aluminium and three peripheral tetrahedral aluminium atoms (Fig. 3). Mehrotra [9] reported that the vapour density measurement showed the vapour to be dimeric.

From the analysis of gaseous and liquid products obtained during pyrolysis, it is likely that the first weight loss of 40% in TG with an endotherm in the DTA is due to the loss of four propylene molecules from one dimer molecule of isopropoxide. The second exotherm in the DTA with the weight loss of 20% in TG is due to the loss of two molecules of isopropyl alcohol.

The aluminium oxide hydroxide formed decomposes to aluminium oxide by losing one mole of water in the subsequent step. The discrepancy in the weight loss in the second decomposition step (i.e., 20% weight loss instead of 28%) is possibly due to the overlap of the third and second exotherms, which makes it difficult to determine the correct value. The final compound is amorphous alumina which on heating to 700°C gives α-alumina.

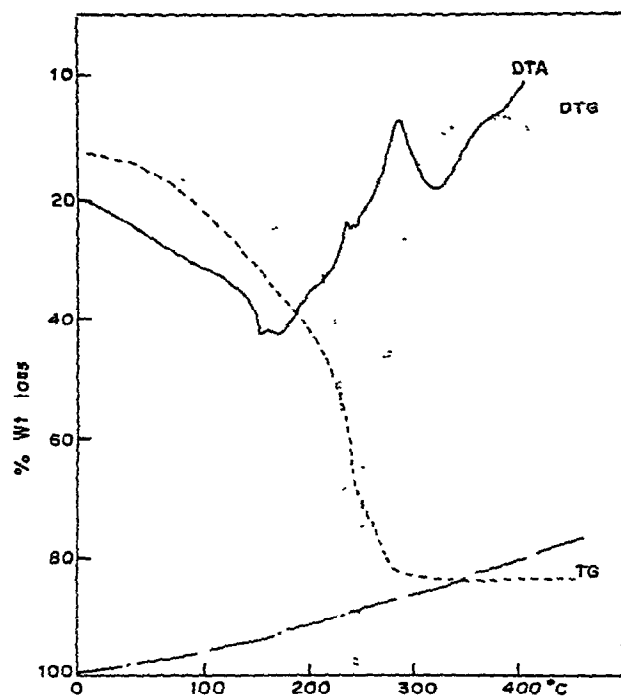On the basis of these results the following possible mechanism for the

Fig. 2. DTA. TG and DTG curves of aluminium isopropoxide.

TABLE 1

Data obtained for aluminium isopropoxide

Nature of the peak in DTA	Temp. range (°C)	Peak temp. (°C)	Wt. loss in TG as % of the original wt.	No. of steps in DTG	Product evolved
Endotherm	40–200	160	40	1	C_2H_6 (4 mole)
Exotherm	200–250	245	20	1	C_3H_7OH (2 mole)
Exotherm	250–300	260	13	1	H_2O (1 mole)
		Total	$\overline{73}$		

TABLE 2

Products obtained in the decomposition of aluminium isopropoxide

Decomposition temp. (°C)	Products collected in trap (1) at 0°C	Products collected in trap (2) at liquid nitrogen temp.
20–200		C_3H_6
200–350	C_3H_7OH	C_3H_6

thermal decomposition of aluminium isopropoxide is proposed.

$$2\,Al(OPr^i)_3 \xrightarrow{200^\circ C} Al_2(OPr^i)_2(OH)_4 + 4\,CH_3-CH{=}CH_2$$

$$\downarrow 250^\circ C$$

$$Al_2(O)_2(OH)_2 + 2\,CH_3-CHOH-CH_3$$

$$\downarrow 330^\circ C$$

$$Al_2O_3 + H_2O$$
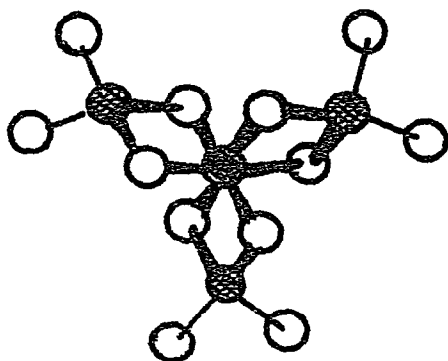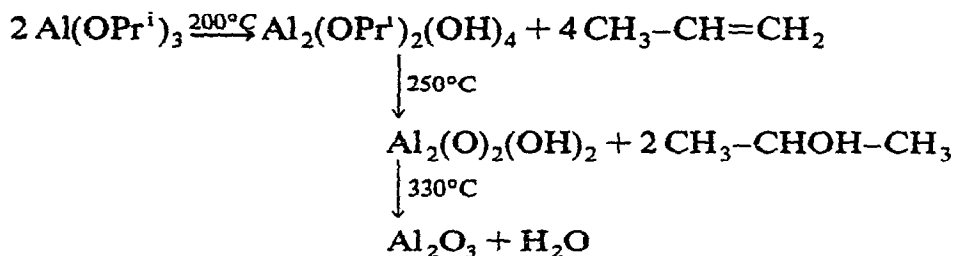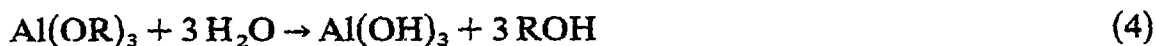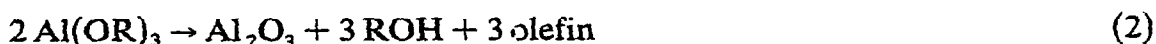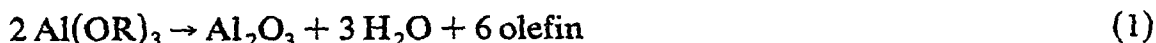
Fig. 3. The structure of $Al(OR_3)_4$. ●, Octahedral Al; ◉, tetrahedral Al; ○, OR.

The mechanism given here differs from that given by Garson et al. [4] in which six possible reactions are proposed

$$2\,Al(OR)_3 \rightarrow Al_2O_3 + 3\,H_2O + 6\,olefin \tag{1}$$

$$2\,Al(OR)_3 \rightarrow Al_2O_3 + 3\,ROH + 3\,olefin \tag{2}$$

$$Al(OR)_3 \rightarrow Al(OH)_3 + 3\,olefin \tag{3}$$

$$Al(OR)_3 + 3\,H_2O \rightarrow Al(OH)_3 + 3\,ROH \tag{4}$$

$$ROH \rightarrow H_2O + olefin \tag{5}$$

$$2\,Al(OH)_3 \rightarrow Al_2O_3 + 3\,H_2O \tag{6}$$

The derivatogram of aluminium isopropoxide shows three steps in DTG and the weight loss in TG is in agreement with the theoretical weight loss determined from our proposed mechanism.

Calcium ethoxide

The derivatogram of calcium ethoxide is shown in Fig. 4. The data obtained from the graph are given in Table 3. The liquid and gaseous products evolved during a separate run have been collected and identified by gas chromatography and mass spectrometry and the findings are given in
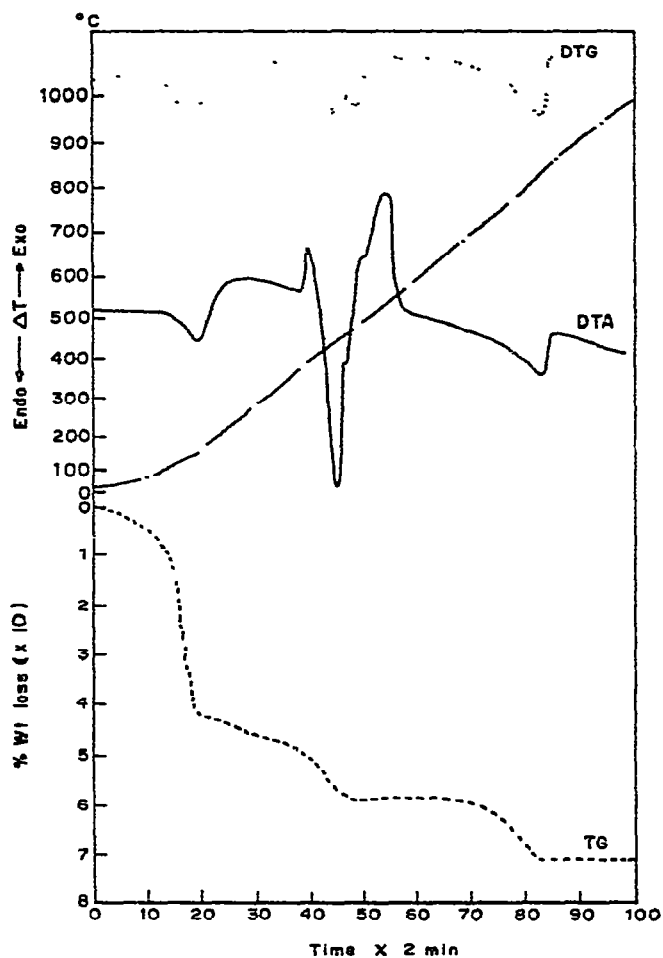
Fig. 4. DTA, TG and DTG curves of crystalline calcium ethoxide

TABLE 3

Data obtained for calcium ethoxide

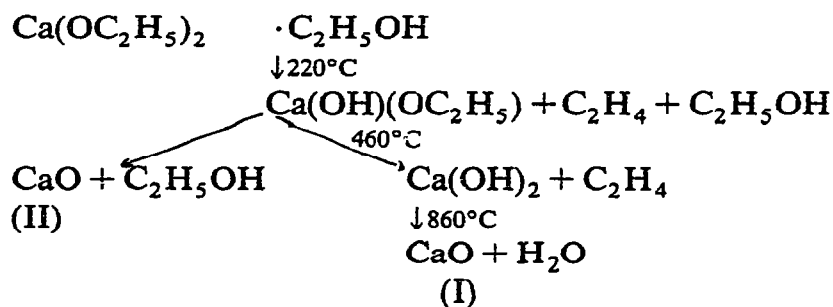| Nature of peak	Temp. range (°C)	Peak temp. (°C)	Wt. loss in TG as % of the original wt.	No. of steps in DTG	Product evolved
Endotherm	120–180	150	42	1	C_2H_5OH (1 mole)
Endotherm	180–300	250	8	1	C_2H_4 (1 mole)
Endotherm	300–450	420	10	1	$C_2H_4 + C_2H_5OH$ (1 mole)
Exotherm	500–600	520			(Small proportion according to step II)
Endotherm	560–860	840	$\underline{10}$	1	H_2O (1 mole)
		Total	$\overline{70}$		

TABLE 4

Products obtained in the decomposition of calcium ethoxide

Decomposition temp. (°C)	Products collected in trap (1) at 0°C	Products collected in trap (2) at liquid nitrogen temp.
30–200	C_2H_5OH	C_2H_4
200–450	C_2H_5OH	C_2H_4
500–850	H_2O	

Table 4. The total weight loss in calcium ethoxide is 70%.

The first weight loss of 42% in TG agrees with the theoretical weight loss of one mole of C_2H_5OH and one mole of C_2H_4 from $Ca(OC_2H_5)_2 C_2H_5OH$. The second weight loss in TG agrees with the loss of the second ethylene molecule from $Ca(OH)(OEt)$. The calcium hydroxide formed during decomposition is stable between 540 and 700°C and shows no weight loss in thermogravimetry. The final weight loss of 10% is due to the loss of a H_2O molecule from $Ca(OH)_2$ which forms CaO.

From the above observation and discussion the following mechanism may be given for the decomposition of calcium ethoxide.

$$Ca(OC_2H_5)_2 \quad \cdot C_2H_5OH$$
$$\downarrow 220°C$$
$$Ca(OH)(OC_2H_5) + C_2H_4 + C_2H_5OH$$
$$\overset{460°C}{\diagup \quad \diagdown}$$
$$CaO + C_2H_5OH \qquad \qquad Ca(OH)_2 + C_2H_4$$
$$(II) \qquad \qquad \qquad \downarrow 860°C$$
$$CaO + H_2O$$
$$(I)$$

Magnesium ethoxide

The derivatogram of magnesium ethoxide is shown in Fig.5. The results of DTA, TG and DTG analysis are given in Table 5. Results of the analysis of the liquid and gaseous products obtained from the decomposition of magnesium ethoxide by gas chromatography and mass spectrometry are liquid product, C_2H_5OH; gaseous product C_2H_4. The DTG curves in this derivatogram show a two-step decomposition. It is observed that magnesium ethoxide decomposes completely at 550°C but the major weight loss occurs below 450°C. It is inferred that the first weight loss of 25% is due to the loss
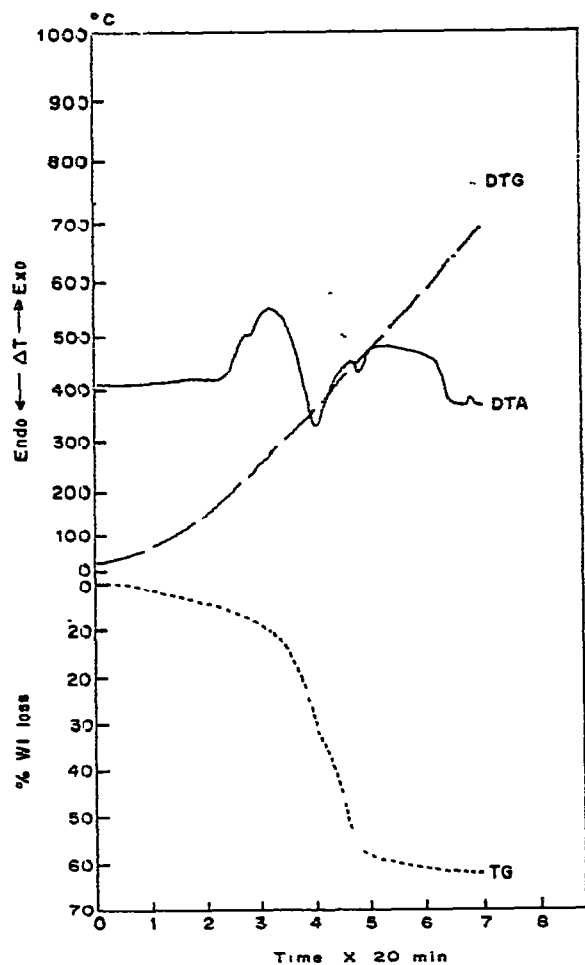
Fig 5. DTA, TG and DTG curves of magnesium ethoxide.

TABLE 5

Data obtained for magnesium ethoxide

Nature of peak in DTA	Temp. range (°C)	Peak temp. (°C)	Wt. loss in TG (as % of the original wt.	No. of steps in DTG	Products evolved
Endotherm	130–330	280	25	1	C_2H_4 (1 mole)
Endotherm	330–420	360	35	1	C_2H_5OH (1 mole)
Endotherm	420–460	450	3		
		Total:	63		

of one ethylene molecule from magnesium ethoxide which is also shown in the DTG. The second weight loss of 35 + 3 in TG and one major and another very small endotherm in DTA are due to the evolution of one ethyl alcohol molecule from one ethoxy group and OH group of the magnesium hydroxyl ethoxide intermediate. This is also shown in the DTG.

From this it is evident that the decomposition of magnesium ethoxide is a two-step reaction

$$Mg(OC_2H_5)_2 \rightarrow Mg(OH)(OC_2H_5) + C_2H_4 \rightarrow MgO + C_2H_5OH$$
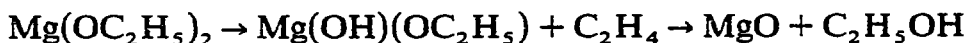
CONCLUSIONS

Aluminium isopropoxide decomposes below 300°C in three steps by losing propylene and isopropyl alcohol and one water molecule.

Calcium ethoxide decomposes below 840°C giving the alcohol and olefin and forming the intermediate stable calcium hydroxide which decomposes to calcium oxide.

Magnesium ethoxide decomposes below 450°C giving one molecule of olefin and one molecule of alcohol.

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