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DIFFERENTIAL THERMAL ANALYSIS STUDY OF VARIOUS OXALATES IN OXYGEN AND NITROGEN

D. DOLLIMORE and D. L. GRIFFITHS

Department of Chemistry and Applied Chemistry, University of Salford, Salford Lancs., U.K.

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Differential thermal analysis (DTA) of some 25 oxalates are reported in atmospheres of oxygen and nitrogen. It is shown that in some cases in nitrogen the metal is formed, in other cases the oxide of lowest valency state is produced, while a third group give the same oxide product in nitrogen and oxygen. The production in oxygen of the oxide for the first group, and of a higher oxide in the second group is a phenomenon which in the first case involves a further reaction of the metal with the oxygen atmosphere. Another group of oxalates produce characteristic DTA curves due to the formation of carbonate as the initial decomposition product. The dehydrations of these oxalates are marked by endothermic peaks.

Thermogravimetry (TG) of a wide range of oxalates in air and in nitrogen has previously been reported [1]. Earlier investigations into the thermal decomposition of oxalates were discussed in that publication. The DTA data by Ugai [2] is characteristic of decomposition in an inert atmosphere with endothermic peaks for the decomposition stage. Doremieux and Boulle [3] report that for some oxalates the decomposition is shifted to a lower temperature when carried out in oxygen but that in other oxalates the decomposition characteristics remain the same in both oxygen and nitrogen.

The DTA technique involves the use of very small quantities of material and the presence of an inert gas allows the observation of the actual decomposition reaction uncomplicated by subsequent or simultaneous oxidation reactions with the atmosphere. The use of oxygen as the carrier gas then demonstrates the changed nature of the reaction.

Since the comparison of DTA results from different sources is to some extent dependent on the type of apparatus and the method of operation, the analysis of some 25 oxalates has been undertaken using a standardized procedure in order that the thermal stability and pattern of decomposition of these single metal oxalates could be studied. This paper is based on an earlier note by the authors presented at the 1st ICTA, Aberdeen 1965 [4].

Experimental and results

Materials

Aluminium oxalate exists in a basic form and has been described in detail in a previous paper [5]. The oxalates $MC_2O_4 \cdot 2\,H_2O$ where $M = Mn^{2+}$, Fe^{2+}, Ni^{2+} and Zn^{2+}, chromium oxalate $Cr_2(C_2O_4)_3 \cdot 6\,H_2O$, iron(III) oxalate $Fe_2(C_2O_4)_3 \cdot H_2O$, copper oxalate $CuC_2O_4 \cdot 1/2\,H_2O$, cadmium, tin(II), lead(II) and thorium(IV) oxalates were the materials studied in the TG study, together with the commercial antimony and bismuth oxalates [1]. Additional high purity oxalates included in this DTA study were those of lithium, sodium, potassium, magnesium, calcium, strontium, barium, ammonium and oxalic acid itself. A commercial sample of cerium(III) oxalate was also used.

Apparatus

The apparatus used was that manufactured by Gebruder Netzsch and operated at a heating rate of 5° min^{-1}. The model No of the DTA unit was 404, the thermocouples were platinum-platinum rhodium, the material was in direct contact with the thermocouple and enclosed by platinum sheaths. To improve base line stability, the sample was diluted to 10% by weight with the reference material and a total weight of 800 mg used throughout the work. The reference material was chromatographic grade alumina calcined at 1200°. The controlled atmosphere consisted of either dry oxygen or dry deoxygenated nitrogen passing over the sample at the rate of 100 ml min^{-1}. At the completion of all analyses in nitrogen, oxygen was admitted to the sample at the maximum temperature, any oxidation of the decomposition product being shown as an exothermic peak.

The results were obtained as graphs of differential temperature and reference temperature against time. The final decomposition products were determined by chemical analysis and X-ray analysis, and checked against the weight loss on the TG data.

Results

Fig. 1 shows a typical DTA curve of an oxalate which first dehydrates (endothermic peak) and then in oxygen shows an exothermic peak at the decomposition temperature but an endothermic peak for decomposition in nitrogen. The decomposition of any carbonate formed in oxygen is endothermic but has the characteristic shape also shown in Fig. 1. This characteristic shape is often not so pronounced in nitrogen. For each type of peak shown in Fig. 1, two temperatures are recorded, the first the point of departure from the base line and the second the peak temperature. Not all the data recorded in this paper is presented in graph form but reference can be made to Fig. 1 when the actual DTA trace is not produced.

Lithium oxalate ($Li_2C_2O_4$) possessed no water of hydration, so the first peak in oxygen was a large exothermic peak ($\Delta T = 14°$) associated with decomposition.

The trace for this and the sodium and potassium oxalates is given in Fig. 2. Similar DTA data for magnesium, calcium, strontium and barium oxalates is given in Fig. 3. Information on the oxalates of aluminium, thorium and cerium is shown in Fig. 4, for chromium and manganese(II) in Fig. 5, for iron(II) and (III) in Fig. 6, and for cobalt and nickel in Fig. 7. The DTA traces for the other oxalates are given in Figs 8–11, viz. copper, zinc and cadmium in Fig. 8, tin and lead in Fig. 9, antimony and bismuth in Fig. 10, and ammonium oxalate and oxalic acid in Fig. 11.

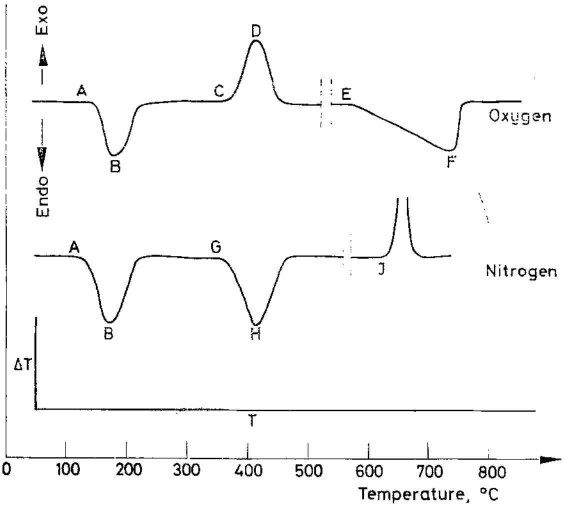
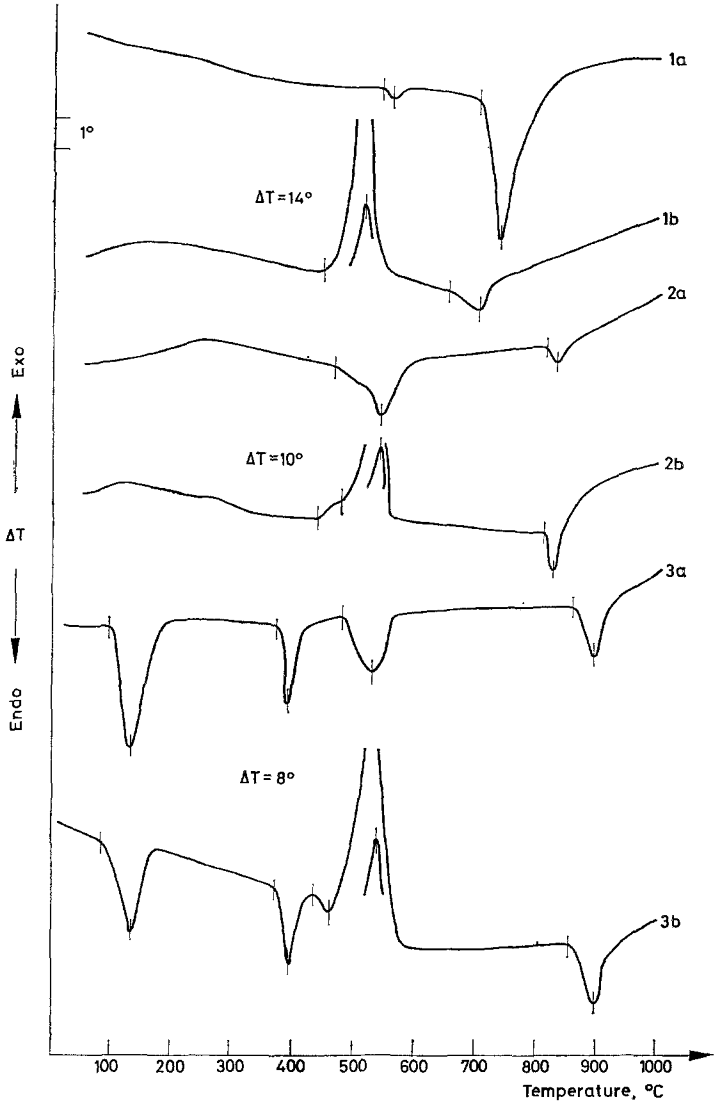


Fig. 1. Typical DTA curves for an oxalate in nitrogen and oxygen. 1. Peak AB: endo dehydration; 2. Peak CD: exo decomposition in oxygen; 3. Peak EF: endo decomposition of the carbonate; 4. Peak GH: endo decomposition in nitrogen; 5. Peak J: an exo peak that sometimes appears when air is admitted at temperature J. (In all the above peaks, the first letter associated with the peak represents the temperature of departure from the base line, the 2nd the temperature at the maximum peak height.)

Discussion

The results may be conveniently divided according to their decomposition pattern in an inert atmosphere and subsequent behaviour on admission of oxygen. Those which on admission of oxygen underwent oxidation of their decomposition products are termed Type I and include oxalates of antimony, bismuth, cadmium, cobalt, copper, iron(II), iron(III), lead, manganese(II), nickel and



tin(II). The other group of oxalates, termed Type II, did not undergo oxidation at the end of the DTA run in nitrogen upon admission of oxygen and these included aluminium, barium, calcium, cerium(III), chromium, lithium, magnesium, potassium, sodium, strontium and zinc.

The following general conclusions can be drawn:

a) All dehydration peaks are endothermic.

b) All primary decomposition peaks in oxygen are exothermic irrespective of whether the product is an oxide or a carbonate.

c) With one exception, viz. copper, all primary decomposition peaks in nitrogen are endothermic.

d) Peaks for the decomposition of the carbonate to the oxide are endothermic both in nitrogen and oxygen and of a characteristic shape.

The endothermic character of all the oxalate decompositions in nitrogen with the exception of copper should be noted, since at least two authoritative texts on thermal decomposition list the thermal decomposition of nickel, lead and thorium oxalates as being exothermic [6, 7]. The inversion of the primary decomposition peak arises from two sources. The compounds of type I show an exothermic peak in oxygen because the oxidation of the initial solid product is strongly exothermic and superimposes on the much weaker decomposition endotherm. The type II compounds show a similar phenomenon because the decomposition results in the formation of carbon monoxide which is oxidized exothermically at the surface. Tests with undiluted samples prove that this effect is not caused by the presence of the reference alumina. This means that a carbonate surface is capable of oxidizing the carbon monoxide in certain cases.

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Fig. 2. DTA curves for the oxalates of lithium (1), sodium (2) and potassium (3) in nitrogen and oxygen

Lithium oxalate

1a	N_2:	538°—553°	endo decomposition to carbonate
		695°—728°	endo decomposition of carbonate
1b	O_2:	444°—511°	exo decomposition to carbonate
		651°—700°	endo decomposition of carbonate

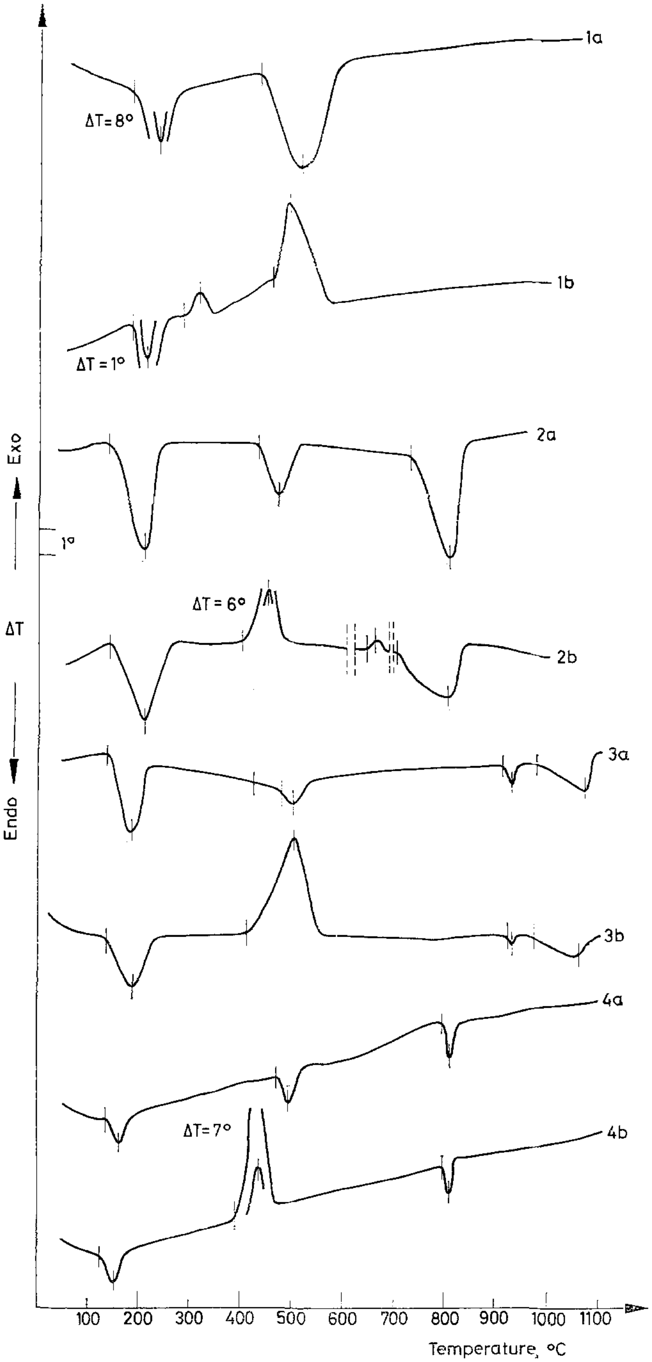
Sodium oxalate

2a	N_2:	464°—541°	endo decomposition to carbonate
		814°—823°	endo melting of carbonate
2b	O_2:	440°—535° (shoulder at 470°)	exo decomposition to carbonate
		812°—823°	endo melting of carbonate

Potassium oxalate

3a	N_2:	95°—132°	endo dehydration
		370°—388°	endo phase transition in oxalate
		481°—525°	endo decomposition to carbonate
		860°—898°	endo melting of carbonate
3b	O_2:	82°—129°	endo dehydration
		370°—388°	endo phase transition in oxalate
		458°—534°	exo decomposition to carbonate
		856°—898°	endo melting of carbonate

(In this and other figures the first temperature quoted is the point of departure from the base line and the second temperature is the temperature at which the maximum in the peak occurs)


1a
ΔT=8°
1b
ΔT = 1°
2a
1°
ΔT = 6°
2b
3a
3b
4a
ΔT=7°
4b
Exo
ΔT
Endo
100
200
300
400
500
600
700
800
900
1000
1100
Temperature, °C

Additional peaks were found due to phase changes and these are listed in Table 1. The phase change in the calcium carbonate was only observed in the sample at 20% dilution. It would seem that there is a possibility of reaction of the carbonate with the alumina diluent.

The class of oxalates listed as Type I contains two distinct sub-groups, namely those that produce a metal in nitrogen as the solid end product and those that

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Fig. 3. DTA curves for the oxalates of magnesium, calcium, strontium and barium oxalates in nitrogen and oxygen

Magnesium oxalate

1a	N_2:	172°— 221°	endo dehydration
		426°— 505°	endo decomposition to oxide
1b	O_2:	182°— 212°	endo dehydration
		279°— 312°	exo
		455°— 486°	exo decomposition to oxide

Calcium oxalate

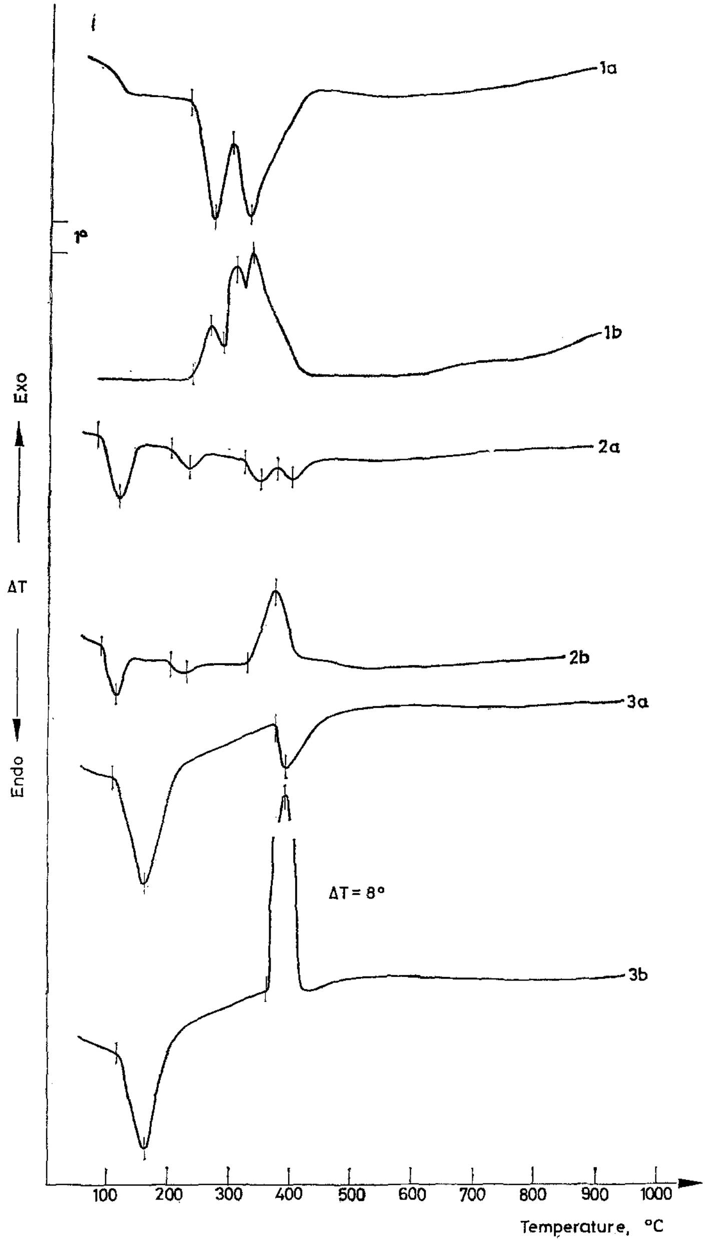
2a	N_2:	134°— 201°	endo dehydration
		425°— 646°	endo decomposition to carbonate
		719°— 797°	endo decomposition to oxide
2b	O_2:	137°— 205°	endo dehydration
		394°— 444°	exo decomposition to carbonate
		643°— 653°	exo phase change in carbonate (shown in sample at 20% dilution)
		698°— 794°	endo decomposition to oxide

Strontium oxalate

3a	N_2:	136°— 184°	endo dehydration
		424°— 501° (shoulder at 468°)	endo decomposition to carbonate
		911°— 924°	endo phase change in carbonate
		980°—1069°	endo decomposition to oxide
3b	O_2:	135°— 185°	endo dehydration
		407°— 502°	exo decomposition to carbonate
		920°— 925°	endo phase change in carbonate
		967°—1057°	endo decomposition to oxide

Barium oxalate

4a	N_2:	132°— 161°	endo dehydration
		468°— 487°	endo decomposition to carbonate
		795°— 802°	endo phase change in carbonate
4b	O_2:	128°— 155°	endo dehydration
		390°— 433°	exo decomposition to carbonate
		795°— 802°	endo phase change in carbonate


1a
1°
1b
2a
2b
3a
3b
ΔT = 8°
Exo
ΔT
Endo
100
200
300
400
500
600
700
800
900
1000
Temperature, °C

produce a lower oxide. On admission of oxygen or air the metal is oxidized to the oxide. An example of this is the thermal decomposition of nickel oxalate. The other group consists of oxalates which decompose in nitrogen to a lower oxide but which oxidize on admission of air or oxygen to a higher oxide. Typical of this class of oxalates is manganese(II) oxalate. Here the oxide MnO is formed but on admission of oxygen this is oxidized to a black oxide in a very strongly exothermic reaction. The subsequent oxidation in both these groups is complete and not superficial because of the high surface area of the initial product and the strongly exothermic character of the oxidation process. In oxidizing up larger quantities of manganese(II) oxide produced by the thermal decomposition of the oxalate the temperature has been observed to rise from ambient to 760°. Surface areas for MnO produced in this way were found to be in the region 20–150 $m^2 g^{-1}$. Similarly nickel produced in this manner by the thermal decomposition of nickel oxalate in nitrogen has large surface areas in the region 100–170 $m^2 g^{-1}$ [9]. The influence of the strongly exothermic oxidation reactions on the decomposition temperature is seen best in the oxalates of manganese, iron, cobalt, nickel and copper. Here the decomposition temperature in oxygen may be much lower than the decomposition temperature in nitrogen; this is because

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Fig. 4. DTA curves for the oxalates of aluminium, thorium, and cerium in nitrogen and oxygen

Aluminium oxalate

1a	N_2:	225°–264°	endo dehydration
		295°–321°	endo decomposition
1b	O_2:	228°–	largely exothermic reaction complex peak
		262°–284°	endo depression, dehydration
		–329°	exo peak decomposition (dehydration and decomposition overlap)

Thorium(IV) oxalate

2a	N_2:	82°–113°	endo dehydration to dihydrate
		201°–228°	endo dehydration to anhydrous salt
		319°–347°	endo } decomposition to oxide
		375°–390°	endo
2b	O_2:	88°–107°	endo dehydration to dihydrate
		200°–223°	endo dehydration to the anhydrous salt
		328°–367°	exo decomposition to oxide

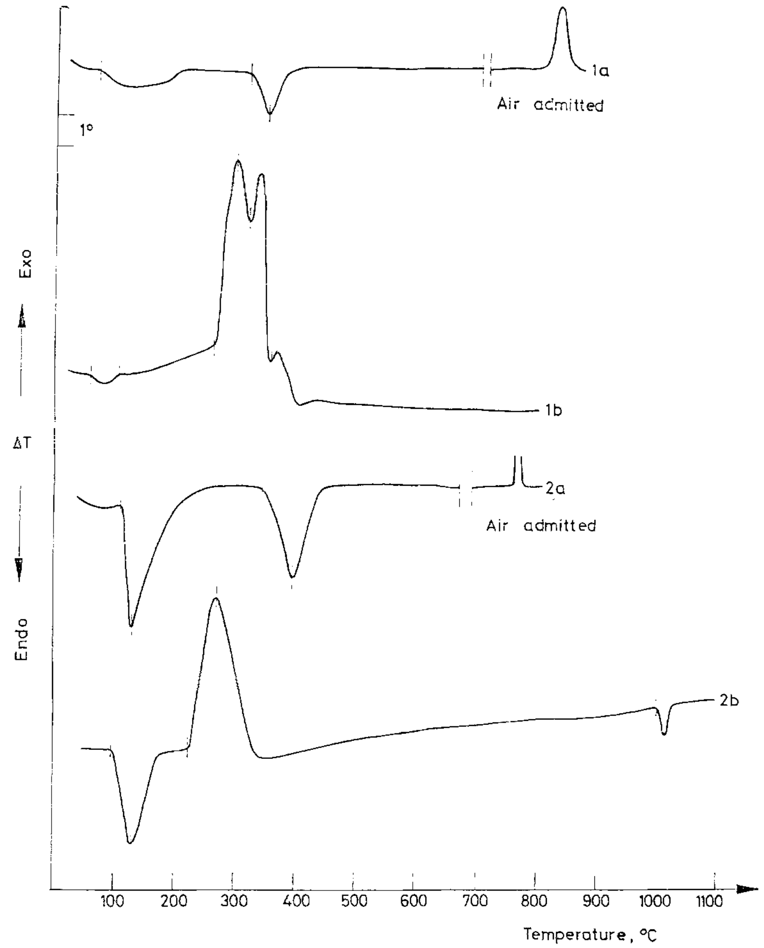
Cerium(III) oxalate

3a	N_2:	109°–159°	endo dehydration
		372°–390°	endo decomposition to oxide
3b	O_2:	113°–159°	endo dehydration
		358°–388°	exo decomposition to oxide

Table 1
Summary of phase changes

Material	Character of peak	Departure from base line °C	Peak temperature °C
Potassium oxalate	endo	370	388
Barium carbonate	endo	795	802
Calcium carbonate*	exo	643	653
Strontium carbonate	endo	920	925
Cobalt oxide	endo	955	968
Manganese oxide	endo	1004	1011
Lead oxide	endo	780	797
		850	857

* See text for observation on this peak.



the initial oxidation of the oxide or metal formed by the thermal decomposition reaction is so exothermic that the subsequent decomposition of unreacted material is accelerated. The oxidation of manganese(II) oxide, and of the nickel metal are good examples. The heat generated by the oxidation of the initial quantities of manganese(II) oxide or nickel formed is sufficient to promote further decomposition of the oxalate. In almost all the other oxalate decompositions the temperature of decomposition in oxygen is either the same as in nitrogen or a little lower.

The initial dehydration reaction is always endothermic. In many dehydrations the product of dehydration is amorphous and the dehydration could be followed by an exothermic recrystallization process. This phenomenon is reviewed at length by Young [10] and it is pointed out that in vacuum and in the presence of very low partial pressures of water vapour the product of dehydration may be amorphous whilst in the presence of larger partial pressures of water vapour the anhydrous product is crystalline [11, 12]. Under these circumstances an exothermic transition should be observed in some cases where an amorphous

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Fig. 5. DTA curves for the oxalates of chromium and manganese in nitrogen and oxygen

Chromium(III) oxalate

1a	N_2:	70°— 123°	endo dehydration
		322°— 349°	endo decomposition to oxide
		800°	exo on admission of air, but not as big as in others where bulk oxidation occurred
1b	O_2:	60°— 103°	endo dehydration
		262°	complex exo, peaks at 295° and 332° separated by minimum at 321°
		355°— 364°	much smaller exo
			both these exothermic regions associated with decomposition to oxide

Manganese(II) oxalate

2a	N_2:	112°— 131°	endo dehydration
		343°— 396°	endo decomposition to oxide
		760°	exo very large, on admission of air at this temperature
2b	O_2:	99°— 127°	endo dehydration
		227°— 269°	exo decomposition to oxide
		1004°—1011°	endo oxide dissociation, not reversible on cooling

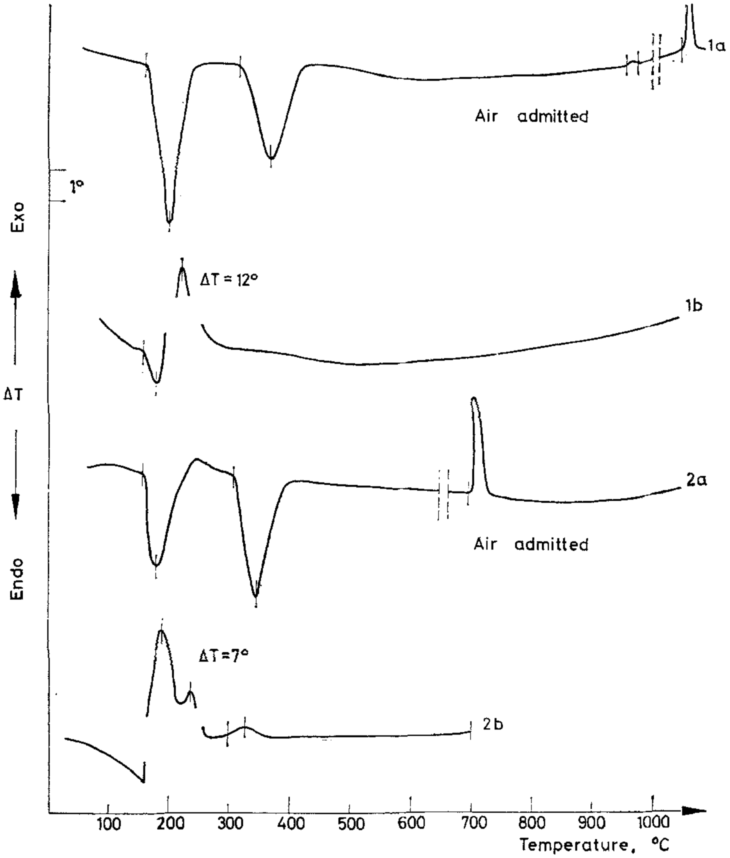


Fig. 6. DTA curves for the oxalates of iron, cobalt and nickel in nitrogen and oxygen

Iron(II) oxalate

1a	N_2:	161°–196°	endo dehydration
		315°–364°	endo decomposition to oxide and metal
		960°–975°	small exo in this region
		1050°–	large exo on admission of air
1b	O_2:	161°–178°	endo dehydration
		178°–221°	exo decomposition to oxide

Iron(III) oxalate

(Data taken from Broadbent, Dollimore and Dollimore [19])

2a	N_2:	163°–182°	endo dehydration	
		291°–345°	endo decomposition	
		700°	large exo on admission of air	
2b	Air:	–159°	endo dehydration	
		–190°	exo	change of valency state and decomposition to oxide
		–240°	subsidiary exo	
		300°–325°	exo	

anhydrous product of dehydration undergoes a recrystallization to a stable crystal form. An endothermic dehydration in an inert dry atmosphere might therefore be expected in some cases to be followed by an exothermic recrystallization, and such exotherms have been reported by Dell and Wheeler [13]. In this study except for the magnesium oxalate no such exotherms could be detected either in dry oxygen or nitrogen. In studies on anhydrous manganese(II) [8], zinc [14] and nickel oxalates [9] reported previously we have shown by X-ray diffraction studies that the anhydrous oxalates prepared by these techniques in dry nitrogen gave clearly distinguishable X-ray diffraction patterns, which indicated that these anhydrous products were crystalline and not amorphous. The difference, between our observations of a crystalline anhydrous salt and those of Topley and Smith [11] and also of Volmer and Seydell [15] who showed the existence of an amorphous anhydrous product in the absence of water vapour, can be explained by the higher temperature range in which our dehydration reactions took place and the presence of a large pressure of inert gas around the sample.

It would seem possible that in a dry nitrogen atmosphere the higher temperature alone of our studies would be sufficient to cause the dehydration to proceed to the stable crystalline form and the exothermic peak associated with recrystallization of an amorphous material is accordingly absent.

There are certain general modes of decomposition for oxalates that can now be listed. Reactions occurring in inert atmospheres are considered first. The first event that can be listed is dehydration which is then followed by oxalate decomposition. The decomposition of the alkali and alkaline earth oxalates is via a stable carbonate stage, e.g.

$$CaC_2O_4 = CaCO_3 + CO$$

At a higher temperature the carbonate may decompose to the oxide with evolution of CO_2. A second group decompose directly to the oxide, viz.

$$MgC_2O_4 = MgO + CO + CO_2$$

and

$$ZnC_2O_4 = ZnO + CO + CO_2$$

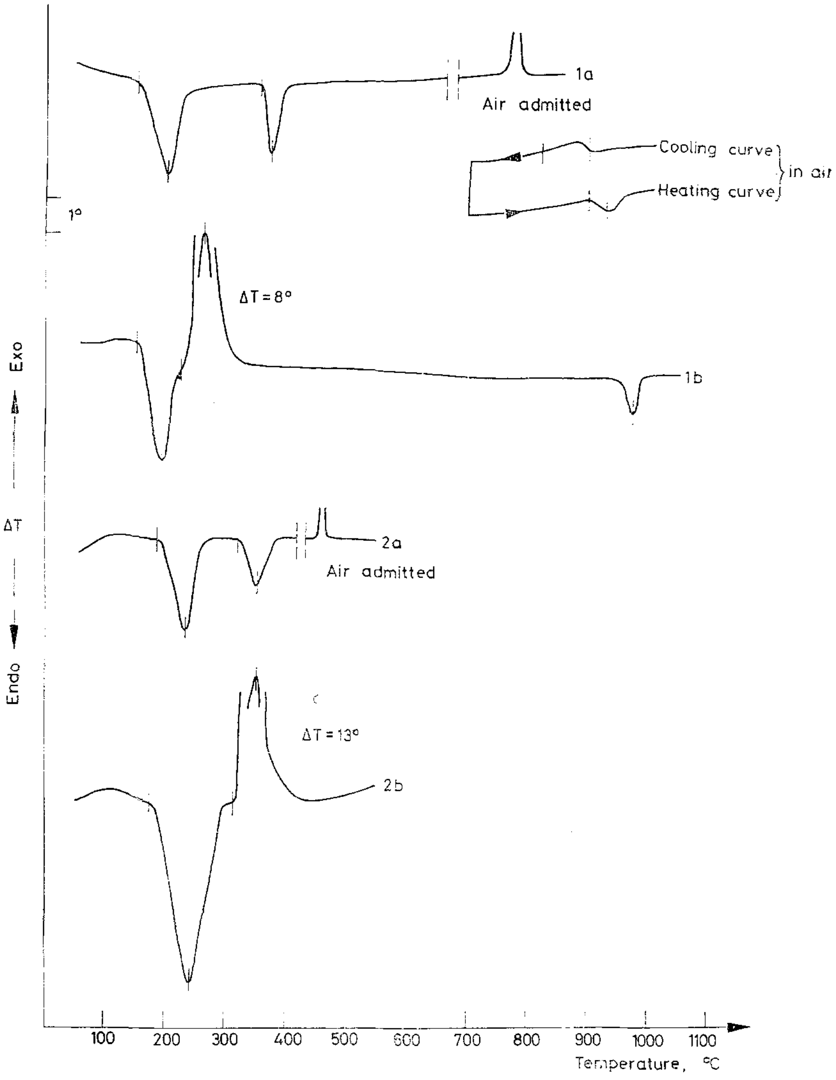
In an inert atmosphere a further group of oxalates decompose to the metal, e.g.

$$NiC_2O_4 = Ni + 2\,CO_2$$

The DTA data discussed in this paper supports the concept of two further reactions taking place in air or oxygen, namely oxidation of a metal or lower oxide, e.g.

$$Ni + \tfrac{1}{2}\,O_2 = NiO$$

and a reaction involving oxygen and product carbon monoxide catalyzed at the solid product surface, e.g.


1a
Air admitted
Cooling curve
Heating curve
in air
1°
ΔT = 8°
1b
Exo
ΔT
Endo
2a
Air admitted
ΔT = 13°
2b
100
200
300
400
500
600
700
800
900
1000
1100
Temperature, °C

$$CO + \frac{1}{2} O_2 = CO_2$$

In other oxalate systems not studied here, namely the rare earth oxalates [16], the residues are given as either carbonates, basic carbonates or oxides and the presence of carbon in the solid residues is also reported due to the surface catalyzed reaction:

$$2\,CO = CO_2 + C$$

The individual oxalates which do not conform to this general pattern may now be discussed.

For aluminium oxalate it has been suggested that the original structure is a three-dimensional array of aluminium, oxalate and hydroxyl ions in a distorted gibbsite lattice and the thermogravimetric (TG) data indicated an overlap of dehydration and decomposition [5]. The DTA data (Fig. 4) showed an endothermic peak due to dehydration and another, partially overlapping, endotherm due to decomposition of the oxalate can be observed for the material run in nitrogen. The overall exothermic nature of the decomposition in oxygen indicates that an overlap of dehydration and decomposition occurs under these conditions.

Thorium oxalate with six molecules of water of crystallization $Th(C_2O_4)_2 \cdot 6\,H_2O$ dehydrates in two stages according to Wendlandt et al. [17]. The intermediate hydrate stage is probably the dihydrate. Srivastava and Vasudeva Murthy [18] describe the subsequent decomposition as proceeding with an endothermic peak in an inert atmosphere to give thorium(IV) oxide and carbon. The sub-

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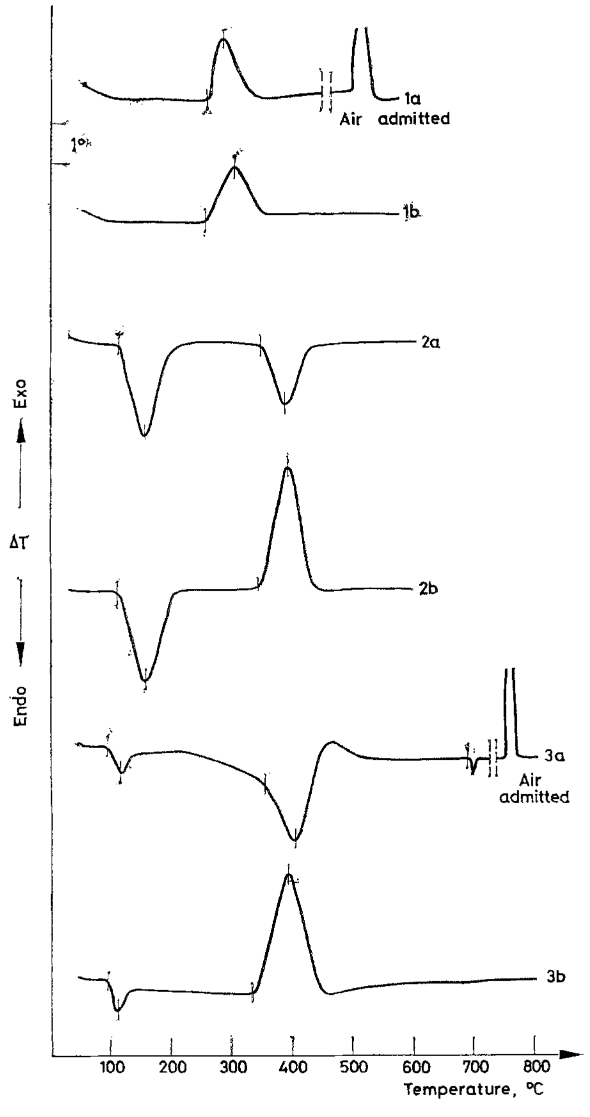
Fig. 7. DTA curves for the oxalates of cobalt and nickel in nitrogen and oxygen

Cobalt oxalate

1a N_2:	149°–197°	endo dehydration
	355°–371°	endo decomposition to metal
	1100°	large exo on admission of air
Cooling curve in air		
	896°–821°	exo $CoO \rightarrow Co_3O_4$
Heating curve in air		
	897°–920°	endo $Co_3O_4 \rightarrow CoO$
1b O_2:	147°–187°	endo dehydration
	219°–261°	exo decomposition
	955°–968°	endo $Co_3O_4 \rightarrow CoO$ (this last is reversible on the cooling curve)

Nickel oxalate

2a N_2:	185°–231°	endo dehydration
	318°–349°	endo decomposition
	450°–	large exo on admission of air
2b O_2:	173°–329°	endo dehydration
	312°–350°	exo decomposition


1a
Air admitted
1°
1b
2a
2b
3a
Air admitted
3b
Exo
ΔT
Endo
100
200
300
400
500
600
700
800
Temperature, °C

sequent oxidation of the carbon then produces the exothermic peak in oxygen and this fits the data produced in this study. A visual inspection of the sample prepared in nitrogen indicated the presence of carbon. Dell and Wheeler [13] suggest that the carbonate is formed as an intermediate but this is not borne out by TG data [1].

The iron(III) oxalate DTA trace in oxygen (Fig. 6) owes its complexity to a change of valency state in the anhydrous oxalate followed by subsequent decomposition to the oxide. Broadbent et al. [19] were able to prepare anhydrous iron(II) oxalate by dehydration of iron(III) oxalate hydrate heated at 220°, and Gallagher and Kurkjion [20] demonstrated the valency change of iron(III) to iron(II) at 250° by use of the Mössbauer effect.

Copper oxalate (Fig. 7) decomposes in nitrogen with an exothermic reaction. In this respect it is similar to the decomposition of mercuric oxalate [2] and silver oxalate [21]. These decompositions are often described as auto catalytic but it is probable that in some environments the results are largely governed by the

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Fig. 8. DTA curves for the oxalates of copper, zinc and cadmium in nitrogen and oxygen

Copper oxalate

1a	N_2:	255°—280°	exo decomposition to metal
		500°—	exo very large on admission of air at this temperature

On taking this run in N_2 up to 1350°:

—1040°	endo due to Cu melting (reversible on cooling at 941° as exo peak)
—1246°	endo peak

1b	O_2:	255°—302°	exo decomposition to oxide

On taking the run in O_2 up to 1150°:

1088°—1102°	endo on cooling
1095°—1081°	exo

Zinc oxalate

2a	N_2:	109°—156°	endo dehydration
		342°—383°	endo decomposition to oxide
2b	O_2:	109°—156°	endo dehydration
		342°—389°	exo decomposition to oxide

Cadmium oxalate

3a	N_2:	88°—110°	endo dehydration
		352°—399°	endo decomposition
		690°—697°	small endo
		750°	large exo on admission of air at this temperature
3b	O_2:	97°—109°	endo dehydration
		334°—388°	exo decomposition

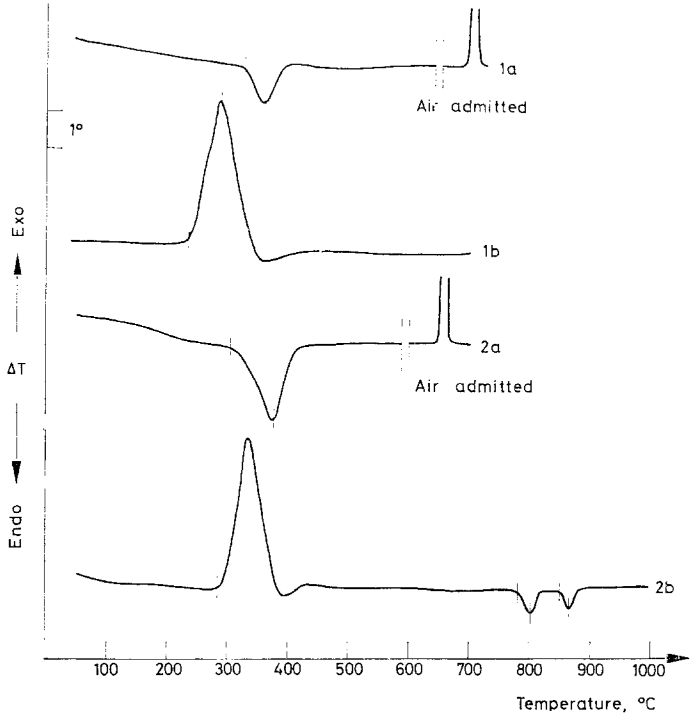

Fig. 9. DTA curves for the oxalates of tin and lead in nitrogen and oxygen

Tin(II) oxalate

1a	N_2:	328°–360°	endo decomposition
		700°	exo very large on admission of air at this temperature
1b	O_2:	235°–292°	exo decomposition to oxide

Lead oxalate

2a	N_2:	304°–375°	endo decomposition
		700°	endo very large on admission of air at this temperature
2b	O_2:	282°–333°	exo decomposition
		780°–797°	endo
		850°–857°	endo

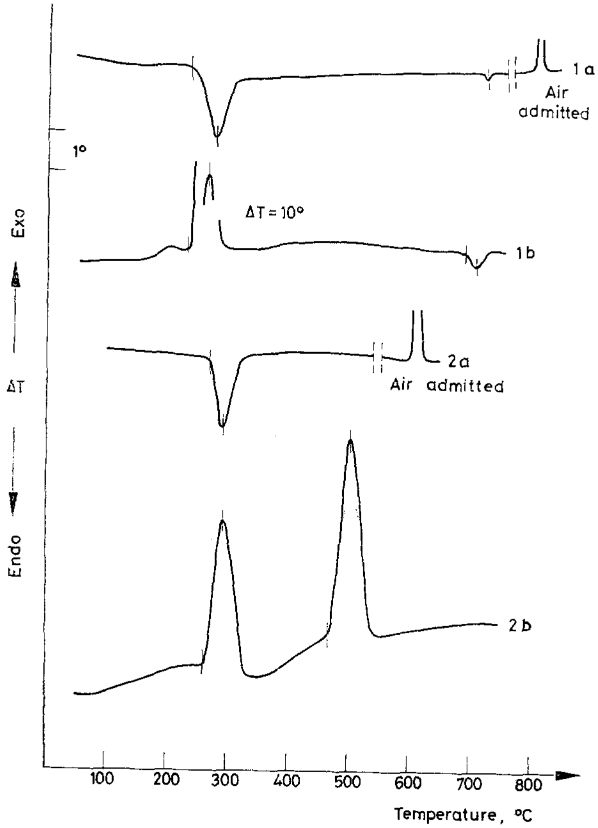

Fig. 10. DTA curves for the oxalates of antimony add bismuth in nitrogen and oxygen

Antimony oxalate

1a	N_2:	267°–288°	endo decomposition
		600°	exo very large on admission of air at this temperature
1b	O_2:	262°–287°	exo decomposition
		468°–496°	exo

Bismuth oxalate

2a	N_2:	243°–274°	endo decomposition
		718°	small endo
		800°	exo very large on admission of air at this temperature
2b	O_2:	230°–265°	exo decomposition
		691°–704°	endo

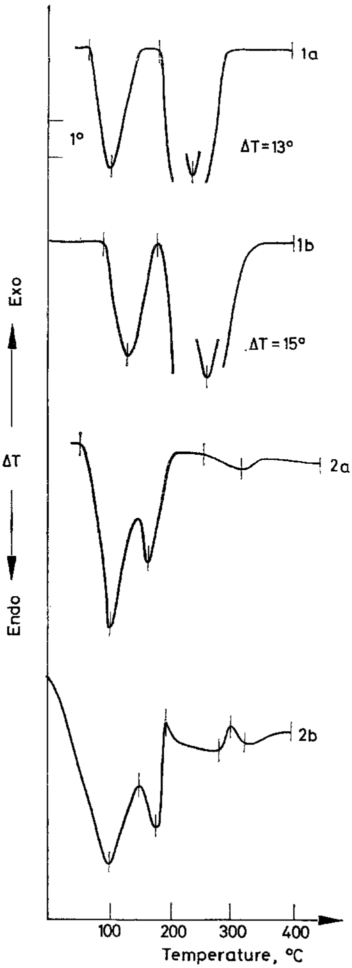

Fig. 11. DTA curves for ammonium oxalate and oxalic acid in nitrogen and oxygen

Ammonium oxalate

1a	N_2:	72°–108°	endo dehydration
		180°–240°	endo decomposition
1b	O_2:	88°–127°	endo dehydration
		178°–260°	endo decomposition

Oxalic acid

2a	N_2:	59°–103°	complex endo subsidiary peak at 165°
		260°–321°	endo
2b	O_2:	ambient-99°	complex endo subsidiary peak at 175°
		188°–278°	endo
		295°	exo
		320°	endo shift

occurrence of self-heating. There is evidence that the presence of oxygen inhibits the decomposition of silver oxalate [22]. The DTA data shows no indication of this for the copper oxalate.

Ammonium oxalate decomposes endothermically and in a similar manner both in nitrogen and oxygen. It occurs as a monohydrate and the first peak is due to dehydration. The decomposition remains endothermic in oxygen because the material is entirely gaseous and there is no active solid product surface to serve as a catalyst for oxidation reactions.

Oxalic acid also shows an overall endothermic reaction in both nitrogen and oxygen and again the DTA trace is similar in both environments. It occurs as a dihydrate and the overall decomposition is an overlapping series of reactions comprising dehydration, volatilization, and decomposition to formic acid and carbon dioxide, all of which could contribute to a largely endothermic DTA trace in both nitrogen and oxygen.

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RÉSUMÉ — On communique les résultats de l'étude de 25 oxalates par analyse thermique différentielle, dans l'oxygène et dans l'azote. On montre que pour certains d'entre eux, dans l'azote, le métal se forme, et que pour d'autres l'oxyde correspondant à la valence la plus faible apparaît; d'autres encore donnent le même oxyde dans l'azote et dans l'oxygène. Dans l'oxygène, et pour le premier groupe, il se forme l'oxyde, tandis que l'oxyde supérieur apparaît pour le second groupe; dans le premier cas, une réaction ultérieure du métal avec l'oxygène de l'atmosphère est mise en jeu. Un autre groupe d'oxalates donne des enregistrements d'ATD caractéristiques en raison de la formation de carbonate comme produit de décomposition initial. Ces oxalates se déshydratent en donnant des pics endothermiques.

ZUSAMMENFASSUNG — Es wurden 25 verschiedene Oxalate durch DTA in Stickstoff- und Sauerstoffatmosphäre untersucht. In einigen Fällen wurde in Stickstoff das Metall gebildet, in anderen das Oxyd von niedrigster Wertigkeit. Es kommt auch vor, daß das gleiche Produkt in beiden Gasen entsteht. Beide erwähnten Produkte werden in Sauerstoff entsprechend oxydiert. Bei einigen Oxalaten erhielt man charakteristische Spitzen, die zeigten, daß das erste Zersetzungsprodukt Karbonat war. Die Dehydration dieser Oxalate zeigte sich durch endothermische Spitzen.

Резюме. — Проведен дифференциальный термический анализ (ДТА) 25 оксалатов в атмосфере кислорода и азота. Показано, что в некоторых случаях металл образуется в азоте, в других случаях окись ниже окисленной формы, а третья группа дает одинаковые продукты окисления в азоте и кислороде. Образование в кислороде окисей, входящих в первую группу и образование высших окисей, входящих в первую группу и образование высших окисей, входящих во вторую группу, является феноменом, который в первом случае включает реакцию металла, проходящую с атмосферой кислорода. Другая группа оксалатов дает характерную кривую ДТА, соответствующую образованию карбоната, являющегося начальным продуктом распада. Процессы дегидратации этих оксалатов характери зуются эндотермическими пиками.