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THERMAL DECOMPOSITION OF BARIUM OXALATE HEMIHYDRATE $BaC_2O_4 \cdot 0.5H_2O$

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ABSTRACT

The thermal behaviour of $BaC_2O_4 \cdot 0.5H_2O$ and $BaCO_3$ in carbon dioxide and nitrogen atmospheres is investigated as part of a study about the thermal decomposition of barium trioxalatoaluminate. For this purpose thermogravimetry, differential thermal analysis, differential scanning calorimetry and high temperature X-ray diffraction were used. An infrared absorption spectrum of $BaC_2O_4 \cdot 0.5H_2O$ was scanned at room temperature.

At increasing temperature, in dry nitrogen, the hydrate water of $BaC_2O_4 \cdot 0.5H_2O$ is split off, followed by the oxalate decomposition. A part of the evolved carbon monoxide disproportionates, leaving carbon behind. At higher temperatures the latter reacts with barium carbonate, previously formed. Finally the residual solid barium carbonate decomposes into barium oxide and carbon dioxide.

In dry carbon dioxide atmosphere an analogous dehydration occurs, followed by oxalate decomposition. Under these conditions the carbon formation is fully suppressed, and as a consequence no secondary reaction occurs. The barium carbonate decomposition is shifted to much higher temperatures, at a low rate in the solid phase, a strongly accelerated one at the onset of melting, and a moderated one when the melt is saturated with barium carbonate. The two phase transitions of $BaCO_3$ are detectable in both atmospheres mentioned.

INTRODUCTION

A substantial knowledge of the thermal behaviour of anhydrous barium oxalate and its thermal decomposition products is required for a correct interpretation of the thermal behaviour of barium trioxalatoaluminate to be studied*.

This contribution deals with the preparation, thermogravimetry (TG), differential thermal analysis (DTA), differential scanning calorimetry (DSC), and high temperature X-ray diffraction (HTX) results of barium oxalate hemihydrate.

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* To be published.

EXPERIMENTAL AND RESULTS

Preparation

A moderately concentrated aqueous solution of 1 mole of $BaCl_2 \cdot 2H_2O$ (U.C.B., pA quality) is added dropwise, with good stirring, to an aqueous solution of 1 mole of $(COOH)_2 \cdot 2H_2O$ (Merck, pA quality). After filtration over a glass filter (G4) the precipitate is extracted with demineralized water in a Soxleth apparatus to remove acid and chloride ions. After drying in air at room temperature the particle size is brought into the range 58–69 μ by mortaring and sieving over a nylon sieve.

ANALYTICAL METHODS (*cf.* ref. 1)

Thermogravimetric results (Fig. 1)

Dehydration

The dehydration results (*cf.* Table 1) are dealt with briefly, because they are less important in view of the oxalatoaluminate decomposition to be studied. Among the hydrates known from the literature (3.5, 2, 1, and 0.5 hydrate[2–4]), only the 0.5 hydrate was observed. It is noteworthy, that a freshly prepared sample possessed a larger water content and a higher temperature range for dehydration, *viz.* 96–140°C, than the sample stored in air for several months before measuring, *viz.* 50–110°C (Table 1). This result, possibly explained by less hamper in the dehydration kinetics of a partly dehydrated lattice, may illustrate the different dehydration temperature ranges found by various authors (Walter-Lévy and Laniepce[2a]: 100–180°C; Peltier and Duval[5]: 76–110°C; Terem and Tüccarbaşi[6]: 120–200°C; Wöhler *et al.*[7]: from 60°C in vacuo).

Oxalate decomposition

a. In dry carbon dioxide atmosphere at ambient pressure (*cf.* Fig. 1a). — Under these conditions the thermal decomposition of anhydrous barium oxalate can be fully described by

$$BaC_2O_4\,(s) \rightarrow BaCO_3\,(s) + CO\,(g).$$

The calculated weight losses (Table 1, expts. a, b, d), and the lack of a subsequent reaction in the temperature range between the oxalate and carbonate decomposition (*cf.* part b of this section) support the proposed decomposition process.

b. In dry nitrogen atmosphere at ambient pressure (*cf.* Fig. 1b). — At this very low, less defined partial pressure of carbon dioxide, disproportionation of carbon monoxide via the well-known Boudouard reaction is likely to occur and has in fact been observed in additional experiments. Therefore the oxalate decomposition is accompanied by carbon formation. The weight contribution of carbon is determined by the actual atmospheric conditions at the reaction interface and therefore by holder

TABLE I[a]

CHARACTERISTIC THERMOGRAVIMETRIC TEMPERATURE VALUES (*T* °C) AND WEIGHT LOSSES (W, μg AND μmol) FOR THE THERMAL DECOMPOSITION OF BaC_2O_4 HYDRATE (A) AND $BaCO_3$ (B).

Experiment	a	b	c	d	e	f
Sample	A	A	A	A	B	B
Sample weight (μg)	6967	8349	8742	7882	8584	8649
Atmosphere	CO_2	CO_2	N_2	CO_2	N_2	CO_2
Dehydration *T*	96–139 (233)[b]	96–157 (235)[b]	50–122[c]	47–107[c]	—	—
W μg	269	318	187	271	—	—
μmol H_2O	14.93	17.68	10.38	15.04	—	…
μmol anhydrous salt	29.71	35.64	37.97	33.78	43.13	43.8
Oxalate decomposition *T*	417–552	415–553	329–548	402–518	—	—
W μg	829	978	1003	941	—	—
μmol CO (calc.)	29.60	34.91	35.79	33.59	—	—
Carbon/carbonate reaction *T*	—	—	596–725	—	—	—
W μg	—	—	237	—	—	—
μmol CO (calc.)	—	—	8.46	—	—	—
Carbonate decomposition *T*	—	—	788–1059	1355–···	703–1059	1348–···
W μg	—	—	1387	—	1863	—
μmol CO_2	—	—	31.52	—	42.33	—
Final temperature of measurement *T*	1206	1203	—	1547[d]	—	—
Residual weight *W* μg	5869	7053	5907	—	6721	—
μmol BaO (calc.)	—	—	38.53	—	43.84	—
μmol $BaCO_3$	29.73	35.73	—	—	—	—

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[a] Heating rate 5°C min^{-1}. $BaCO_3$, Merck pA quality, sample treatment analogous to BaC_2O_4 hydrate. [b] Only a few μg H_2O was lost above the first procedural final temperature mentioned. [c] This sample was already partially dehydrated. [d] A continuous weight loss occurs on isothermal operation at this temperature.

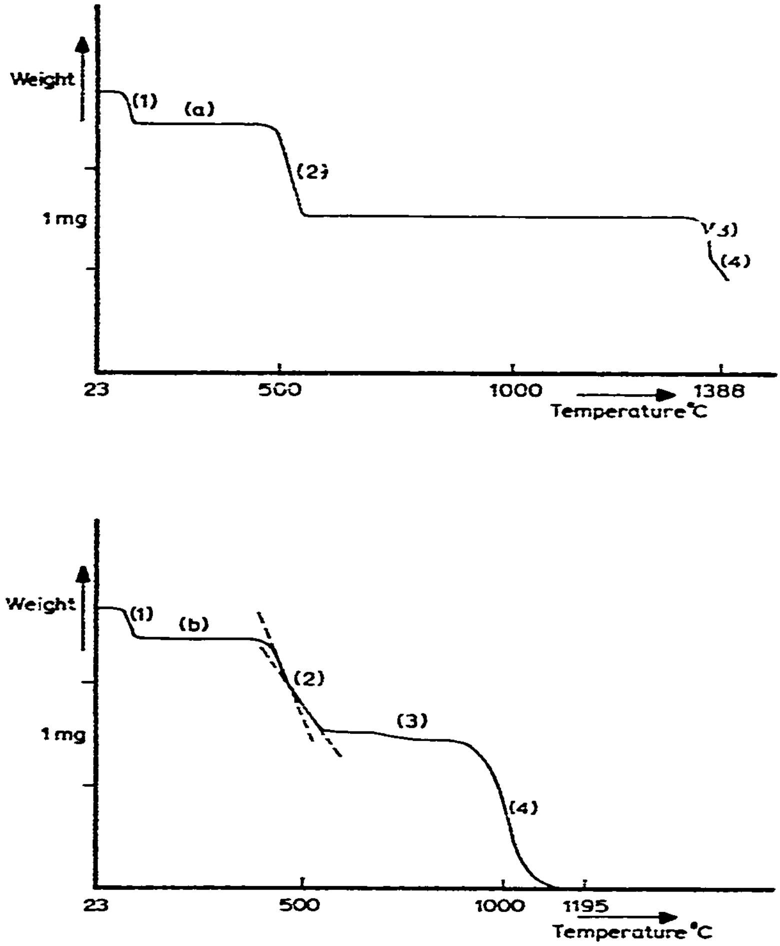

Fig. 1. Survey TG thermogram of $BaC_2O_4 \cdot 0.5H_2O$. Heating rate, 5 °C min^{-1}; sample holder, Pt, internally coated with Rh. Sample weight, 5–10 mg. (a) atmosphere, dry carbon dioxide; flow rate, 34 cc min^{-1}; pressure, atmospheric. (1), Dehydration; (2), oxalate decomposition; (3), carbonate decomposition (melting phase); (4), carbonate decomposition (partly molten phase). (b) atmosphere, dry nitrogen; flow rate, 28 cc min^{-1}; pressure, atmospheric. (1), Dehydration; (2), oxalate decomposition, overlapped by Boudouard reaction; (3), reaction of carbon and carbonate; (4), carbonate decomposition (solid phase).

geometry, flow rate, heating rate and other experimental parameters. The onset of carbon formation is determined by kinetical and topochemical conditions such as availability of nucleation sites.

Thermodynamically the equilibrium lies to the carbon (graphite) side in the temperature range under consideration (*cf.* Fig. 2a). Only a large CO_2/CO pressure ratio hampers carbon formation (*cf.* part a of this section). The decrease in the procedural starting temperature of the decomposition (~410 °C in carbon dioxide, versus 329 °C in nitrogen) is remarkable, whilst the procedural final temperature values were not found to be much different (~550 °C).

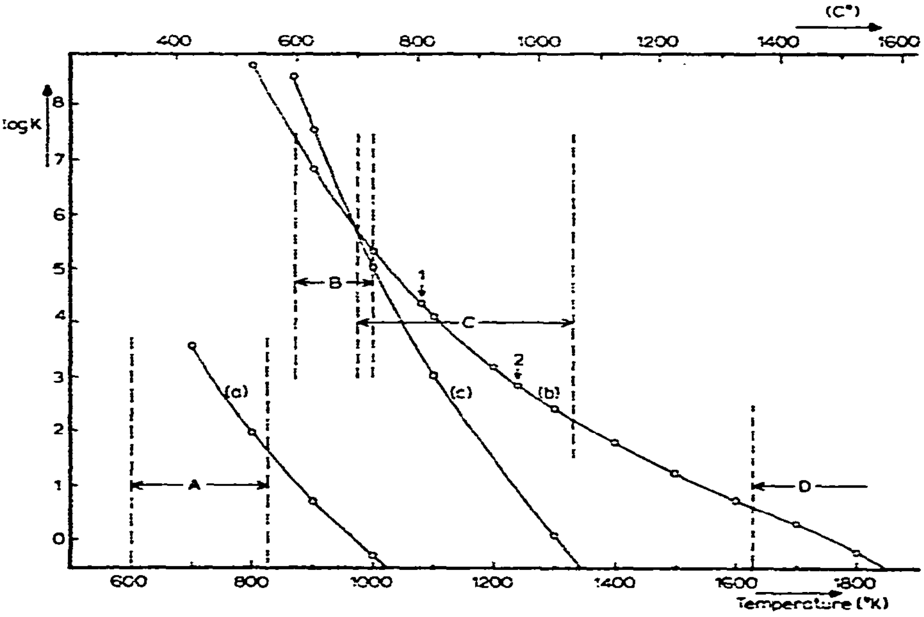

Fig. 2. Negative logarithm of the equilibrium constant K as a function of temperature for the following equilibria (*cf.* data Table 2). (a) C(graphite)+CO_2(g)$\rightleftharpoons$2CO(g) (b) $BaCO_3$(s)$\rightleftharpoons$BaO(s)+CO_2(g) (c) $BaCO_3$(s)+C(graphite)$\rightleftharpoons$BaO(s)+2CO(g). The temperature ranges of the subsequent steps found in the thermal decomposition of BaC_2O_4 are given for nitrogen of atmospheric pressure: A, oxalate decomposition (330–550 °C); B, carbon/carbonate reaction (600–725 °C); C, carbonate decomposition (790–1060 °C, for pure $BaCO_3$: 705–1060 °C). For carbon dioxide of atmospheric pressure: D, carbonate decomposition (from 1350 °C). 1 (806 °C) and 2 (968 °C) are phase transitions of $BaCO_3$.

The following sequence of reaction steps covers the experimentally observed TG curve quite satisfactory (temperature ranges indicated):

BaC_2O_4 (s) → $BaCO_3$ (s)+CO (g) ; 330–470–550 °C (i)

2CO (g) → C (s)+CO_2 (g) ; 470–550 °C (a)

$BaCO_3$ (s)+C (s) → BaO (s)+2CO (g); 600–725 °C (c)

Between 330 and 470 °C, only (i) proceeds with a detectable rate. On the other hand (a), though thermodynamically favoured, is kinetically inhibited at these relatively low temperatures. At 470 °C, (a) becomes observable by virtue of kinetically more favourable conditions such as nucleation rates and increasing unbalance between local CO production and diffusive off-transport velocities. The competitive effect of (a) next to (i) is reflected in the abruptly decreasing slope of the TG curve at 470 °C: Fig. 1b at (2). At 550 °C the decomposition of the oxalate is complete. This marks the termination of (i) and (a) but some graphite is still present in the $BaCO_3$ sample. At higher temperatures thermodynamical conditions for reaction (c) become increasingly favourable: Fig. 2, curve (c). Although the first weight loss (*cf.* Table 1, expt. c) is detectable already at 600 °C, the main effect is seen between 670 and 725 °C.

According to Fig. 2 the equilibrium pressures $p(CO)$ corresponding to (c) are: $10^{-4.1}$ atm. at 600 °C; $10^{-3.3}$ atm. at 670 °C; $10^{-2.7}$ atm. at 725 °C, *i.e.*, sufficiently large so as to allow observable off-transport rates. Disproportionation of CO is thermodynamically disfavoured in this temperature range as can be seen in Fig. 2, curve (a). The weight loss (*cf.* Table 1, expt. c) is in reasonable accordance with the proposed reaction sequence.

It should be noted that the partial pressure of CO_2 in the nitrogen flow is very small*. This is illustrated by the low procedural starting temperature for the decomposition of initially *pure* $BaCO_3$ in the nitrogen atmosphere: 703 °C (Table 1, expt. e). Using the $BaCO_3$ dissociation data of Stern and Weise[9] as represented in Fig. 2 curve (b), this yields $p(CO_2) = 10^{-5.8}$ atm. Thermodynamically this low $p(CO_2)$ value is "provocative" to initiate the reaction (a). However, after the termination of (i) and (a) the effective (local) CO_2 pressure at the freshly formed $BaCO_3$ surface will be higher than the former value because of the inevitably slow rate of diffusion. Thus the thermal decomposition of $BaCO_3$ obtained from BaC_2O_4 may be expected to start at a higher temperature than 703 °C, as in fact is observed (see next section).

The differences between the results obtained by other authors are due to different or poor atmosphere control: Walter-Lévy and Laniepce[2] in air: α-BaC_2O_4 stable to 400 °C, from 400 °C β-BaC_2O_4, $BaCO_3$ and a small carbon formation with kinks in the TG curve; Peltier and Duval[5]: air, 346–476 °C. $BaCO_3$ formation with a kink at 411 °C; Terem and Tüccarbaşi[6]: air, slight decomposition 320–340 °C, intermediate oxalatocarbonates between 340 and 420 °C supposed; Wohler *et al.*[7]: vacuum, $BaCO_3$ formation from 425 °C.

The only measurement of the barium oxalate decomposition in a nitrogen atmosphere originates from Paulik *et al.*[10]. The qualitative picture of their TG curve is in reasonable agreement with our results, though their characteristic temperatures are shifted to higher values due to their atmospheric control and weight sensitivity. Their statement, that "thermogas-titrimetry" experiments are necessary for the elucidation of the thermal decomposition of barium oxalate in nitrogen atmosphere is incorrect. A simple thermogravimetric control in carbon dioxide atmosphere is a good alternative for their intricate titrimetric gas analysis method as is shown by our results.

Carbonate decomposition

The observed procedural starting temperatures of the $BaCO_3$ decomposition

$$BaCO_3\,(s) \rightarrow BaO\,(s) + CO_2\,(g) \qquad \text{(b)}$$

confirm the expected dependency on CO_2 partial pressure. (703 °C in dry nitrogen; 788 °C in dry nitrogen with preceding CO_2 production by the Boudouard reaction; 1348 °C at atmospheric CO_2 pressure.)

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*Prepared free from carbon dioxide by means of KOH pellets.

TABLE 2

DATA OF LOG *K* AT DIFFERENT TEMPERATURES FOR SOME EQUILIBRIA INVOLVED IN THE THERMAL DECOMPOSITION OF ANHYDROUS BARIUM OXALATE

Reaction	*Temperature (°K)*									
	400	*500*	*600*	*700*	*800*	*900*	*1000*	*1100*	*1200*	*1300*
$C(graphite)+CO_2(g)\leftrightarrows 2CO(g)$[8]	−13.27	− 8.75		−3.57	−1.96	−0.72	+0.28	+1.09		+2.32
$BaCO_3(s)\rightleftharpoons BaO(s)+CO_2(g)$[9]	−26.20	−19.19	−14.53	−11.22	−8.76	−6.84	−5.33	−4.12	−3.19	−2.41
$BaCO_3(s)+C(graphite)\leftrightarrows BaO(s)+2CO(g)$	−39.47	−27.94		−14.79	−10.72	−7.56	−5.05	−3.03		−0.09

As a result different temperature values are given by other authors: no weight change till 875°C[5], 920°C[10], 1000°C[11]. Wöhler *et al.*[7] found the carbonate decomposition starting in vacuo at 650°C. Hancock and Sharp[12] obtained kinetical information about the carbonate decomposition from measurements on loose powder in vacuo from 738–808°C and on pellets in nitrogen in the temperature range 961–1035°C proceding by a diffusion mechanism (961–1009°C) and a phase boundary mechanism (1016–1035°C). Measurements on bulk quantities at atmospheric pressure were carried out by Hedvall[13], resulting in sintering (1200–1300°C) and melting (fully at 1360°C with strong CO_2 effervescence).

The effervescence stops at 1425°C though at 1550°C carbon dioxide is still present in the melt. Baker[14] studied the system BaO/CO_2 in the pressure range 0.001–450 atm. By means of thermogravimetric measurements at isobaric conditions

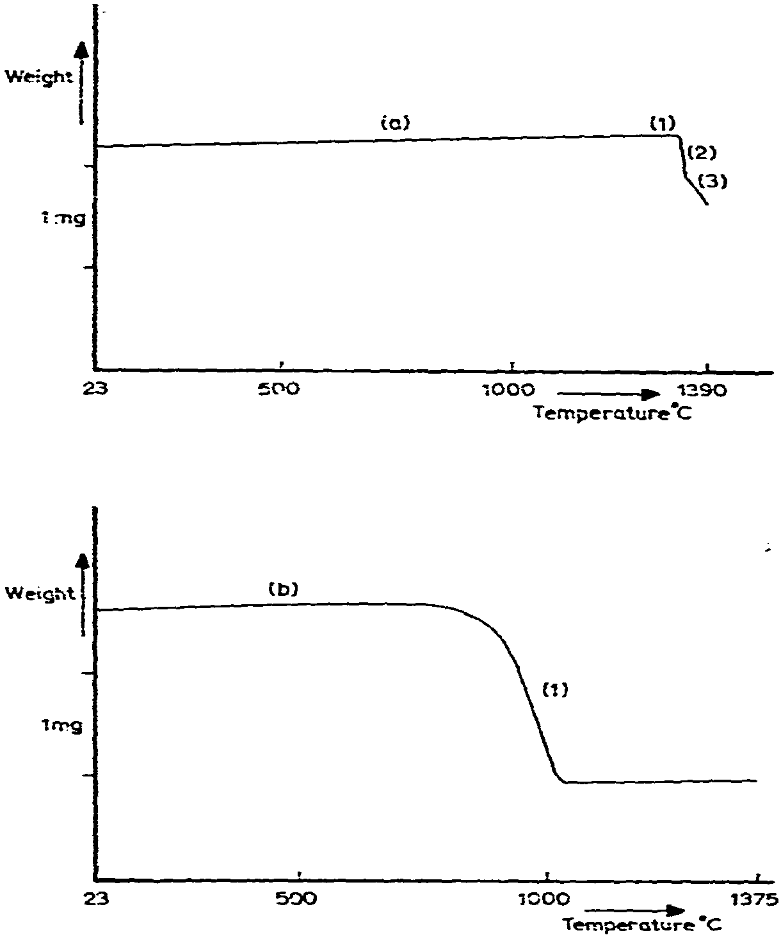

Fig. 3. Survey TG thermogram of $BaCO_3$. Heating rate, 5°C min^{-1}. Sample holder, Pt, internally coated with Rh. Sample weight, 5–10 mg (a) atmosphere, dry carbon dioxide; flow rate, 54 cc min^{-1}; pressure, atmospheric. (1), Carbonate decomposition (solid phase); (2), *idem* (melting phase); (3), *idem* (partially molten phase). (b) atmosphere, dry nitrogen; flow rate, 28 cc min^{-1}; pressure, atmospheric. (1), Carbonate decomposition (solid phase).

he found points of detectable decomposition, shifted to lower temperature values at decreased carbon dioxide pressure. At continued heating first a solid solution of BaO in $BaCO_3$ was formed. This was followed by melting to a composition saturated with respect to $BaCO_3$. Further heating of the partly molten material was accompanied by successive losses of carbon dioxide (Data: eutectic point: 1060°C; 0.00661 atm.; 64 mole % $BaCO_3$. Melting point BaO: 1925°C. Melting point $BaCO_3$: 1555°C. Fusion temperature of $BaCO_3$ at 1 atm.: 1360°C).

Our measurements on pure $BaCO_3$, and on $BaCO_3$ resulting from the decomposition of BaC_2O_4, agree very well (*cf.* Table 1, Figs. 1 and 3). At low partial pressure the material evolves CO_2 mainly from the solid phase. In nitrogen atmosphere: temperature range 788–1059°C *i.e.*, below the reported eutectic temperature of 1060°C[14], whilst at higher CO_2 pressure more CO_2 is given off from the melt of $BaCO_3$ and BaO. (Our result for CO_2 at 1 atm.: temperature range of weight loss 1348–... °C *i.e.* near the fusion temperature of 1360°C at 1 atm. found by Baker[14].) In conclusion, our results agree fairly well with those of Hedvall[13] and Baker[14].

DIFFERENTIAL THERMAL ANALYSIS RESULTS (*cf.* Fig. 4, Table 3)

The dehydration shows the expected endothermal peak. The oxalate decomposition is found to proceed possibly in a two step mechanism, in nitrogen atmosphere as well as in carbon dioxide atmosphere. In both cases a shoulder on the endothermal peak is found (506°C resp. 537°C). The two phase transitions of $BaCO_3$ are measured at 812°C and ~970°C. They are detectable thanks to the slow carbon dioxide removal resulting from the DTA sample holder geometry.

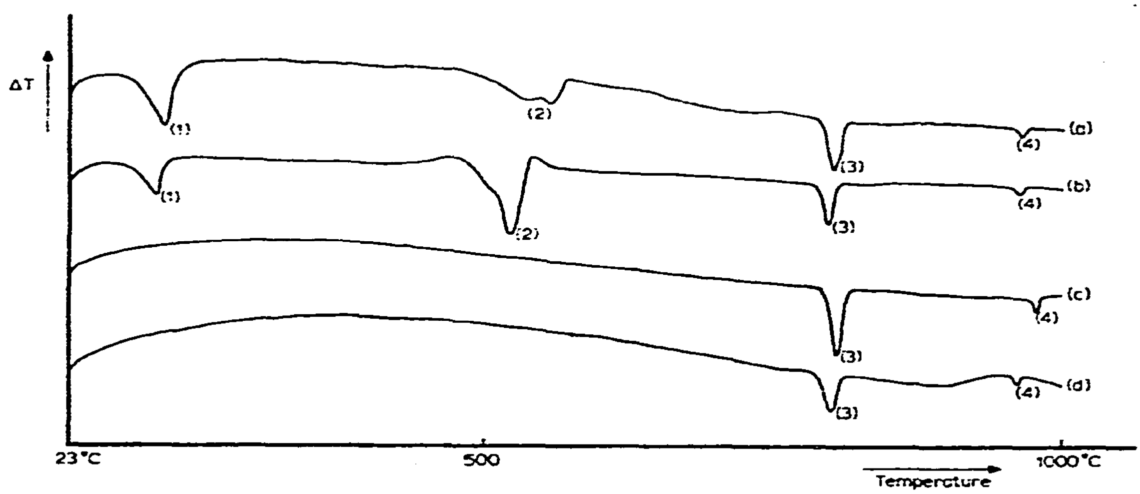

Fig. 4. DTA thermograms of $BaC_2O_4 \cdot 0.5H_2O$ (a, b) and $BaCO_3$ (c, d) scanned in carbon dioxide (a, c) and nitrogen (b, d) atmosphere. Heating rate, 10°C min^{-1}; α-Al_2O_3 between sample and thermocouple; pressure, atmospheric; dry carbon dioxide, flow rate, 34 cc min^{-1}; dry nitrogen, flow rate, 28 cc min^{-1}. (1), Dehydration; (2), oxalate decomposition; (3), phase transition; (4), phase transition.

TABLE 3

COMPARISON OF THE DIFFERENTIAL THERMAL ANALYSIS RESULTS OF BaC_2O_4 HYDRATE AND $BaCO_3$ OBTAINED BY DIFFERENT AUTHORS[a]

	BaC_2O_4 hydrate (ref. 15)	*$BaC_2O_4 \cdot H_2O$ (ref. 16)*		*BaC_2O_4 (ref. 2)*				*$BaCO_3$ (ref. 9)*	*This work*			
				$0.5H_2O$	*$1H_2O$*	*$2H_2O$*	*$3.5H_2O$*		*$BaC_2O_4 \cdot 0.5H_2O$*		*$BaCO_3$*	
Atmosphere	N_2	N_2	vacuum	air[b]	air[b]	air[b]	air[b]	—	N_2	CO_2	N_2	CO_2
Dehydration	132–161	183	118	170	185	130 195	80 135 195	—	113–153	99–158	—	—
Oxalate decomposition	468–487	530	498	490 540	470 525	460 490 545	460 535	—	474–526	476–561	—	—
Phase transition	795–802	—	—	800[c] 750[d]	— —	— —	— —	803[c] 750[d]	783–811	798–812	794–811	800–814
Phase transition	—	—	—	950[c] 915[d]	— —	— —	— —	976[c] 955[d]	964–969	961–967	959–965	970–978

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[a] Single data are peak temperatures. Among the data combined by a hyphen the first value represents the onset temperature and the second is the peak temperature. [b] As a consequence of the atmosphere conditions the exothermal oxalate decomposition peaks cannot be compared with the endothermal peaks mentioned by the other authors. [c] The phase transition exhibits a pronounced hysteresis. These are the data found at increasing temperature. [d] Value at decreasing temperature.

The use of α-Al_2O_3 for thermocouple shielding is allowed in DTA. There is a poor contact between $BaCO_3$ and Al_2O_3 particles ($BaCO_3$ layer on Al_2O_3) and the heating rate used in DTA is a factor 2 larger than in TG measurements. Moreover a TG measurement on a normally pretreated and thoroughly mixed sample of $BaCO_3$ and α-Al_2O_3 (molar ratio 3:1) gave the following temperature ranges for weight loss: 698–1053 °C in N_2 atmosphere and a range from 813 °C on in CO_2 atmosphere. In a nitrogen atmosphere the sample (5–10 mg) has reached a weight loss of ~200 μg at ~820 °C, followed by a larger linear weight loss till ~970 °C, and finished by a less strong linear weight loss till constant weight at 1053 °C. In CO_2 atmosphere *ca.* 100 μg weight loss occurs till 1010 °C, followed by a short larger weight loss and a long linear weight loss (~300 μg). At 1297 °C an initial strong acceleration analogous to the behaviour of pure $BaCO_3$, is followed by a linear weight loss till the end of the measurement (1482 °C). Much carbon dioxide is still present in the reaction mixture.

A supplementary conclusion from this TG measurement may be, that under conditions of intimate contact $BaCO_3$ is involved in a slow solid–solid reaction with α-Al_2O_3. In nitrogen atmosphere it is probably fully superseded by its own decomposition, at all events not to be distinguished from the reaction with α-Al_2O_3 by TG measurement. In CO_2 atmosphere the procedural starting temperature of the CO_2 production is substantially lowered by the presence of Al_2O_3, and a distinction with the decomposition of pure $BaCO_3$ by means of a TG measurement can be made.

A second conclusion may be, that around the phase transitions an increase in the reactivity of $BaCO_3$, enhancing the CO_2 production rate is measurable.

The results of the DTA experiments are in reasonable agreement with those of other authors, as can be expected from the less sensitive atmosphere control inherent to this method (*cf.* Table 3).

DIFFERENTIAL SCANNING CALORIMETRY RESULTS (*cf.* Fig. 5, Table 4)

The DSC results are in reasonable agreement with the results reported in the preceding section. As a consequence of the different holder geometry the characteristic dehydration temperatures are shifted in the lower temperature direction. The DSC thermograms show a different pattern in the oxalate decomposition (an exothermal

TABLE 4

DIFFERENTIAL SCANNING CALORIMETRY RESULTS (r.t.–600 °C) FOR $BaC_2O_4 \cdot 0.5H_2O$ IN CO_2 AND N_2 ATMOSPHERES

	Atmosphere	*Onset temperature (°C)*	*Peak temperature (°C)*
Dehydration	CO_2	48	142
	N_2	52	128
Oxalate decomposition	CO_2	454	494 (*exo*) 539 (sh. *endo*) 572
	N_2	438	471 (*exo*) 515

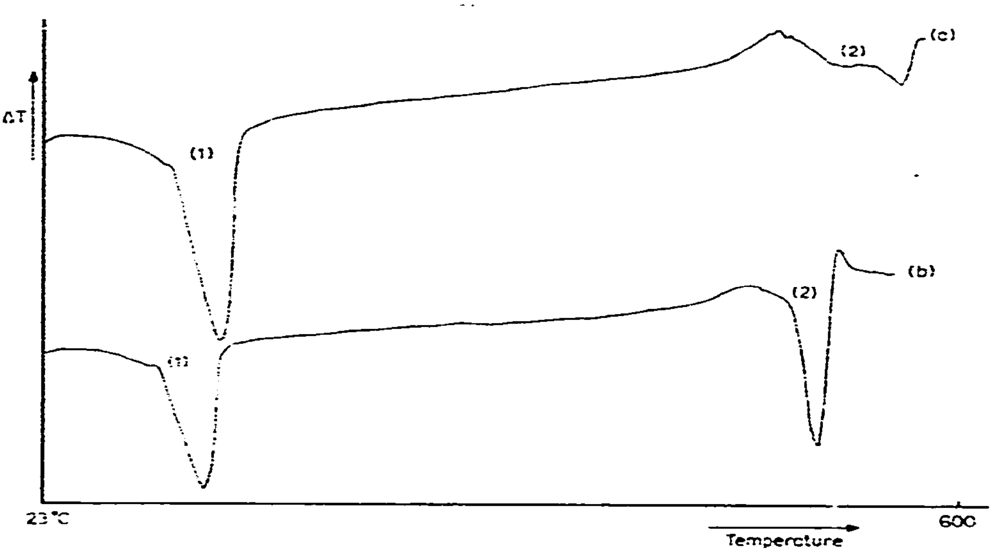

Fig. 5. DSC thermograms of $BaC_2O_4 \cdot 0.5H_2O$ scanned in carbon dioxide (a) and nitrogen atmosphere (b). Heating rate, 10°C min^{-1}; pressure, atmospheric; atmosphere, dry carbon dioxide, flow rate, 34 cc min^{-1}; dry nitrogen, flow rate, 28 cc min^{-1}. (1), Dehydration; (2), oxalate decomposition.

effect at the onset in both atmospheres and absence of a shoulder in the nitrogen case). The residual powder was grey in the nitrogen case; in carbon dioxide it was white on places with good and black on places with poor atmosphere contact. Again the characteristic temperatures were found to be lower under nitrogen than under carbon dioxide atmosphere.

HIGH TEMPERATURE X-RAY DIFFRACTION RESULTS

Initially $BaCO_3$ and $BaC_2O_4 \cdot 0.5H_2O$ were scanned with a low heating rate (0.01–0.02°C min^{-1}) in a nitrogen atmosphere (<10 ppm CO_2) at atmospheric pressure*. For $BaCO_3$ a phase transition was found in the range 796–824°C. In the range 851–877°C a new phase was formed. The majority of its characteristic reflections persisted in the high temperature range (BaO was formed under these experimental conditions). The phase transition of the remaining $BaCO_3$ was scarcely visible at 977°C. $BaCO_3$ fully vanished at 1036°C.

$BaC_2O_4 \cdot 0.5H_2O$ showed its dehydration in the range 102–120°C, followed by the formation of a new phase at 343°C, which latter phase had vanished at 391°C (perhaps the transition α-$BaC_2O_4 \rightarrow \beta$-$BaC_2O_4$ at 400°C, as reported by Walter-Lévy and Laniepce[2]). At the same time at 343°C the intensive lines of $BaCO_3$ became visible. Very weak lines, which were not present at $BaCO_3$, showed a transition in the range 652–666°C. At 706°C weak BaO lines were formed.

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*In our other thermal analysis measurements nitrogen was made free of carbon dioxide by means of KOH pellets. Much higher heating rates were used (TG: 5°C min^{-1}; DTA: 10°C min^{-1}; DSC 10°C min^{-1}).

In a carbon dioxide atmosphere $BaC_2O_4 \cdot 0.5H_2O$ gave the following results; dehydration: 94–115 °C; oxalate decomposition: 387–433 °C; no phase transition in the temperature range <600 °C.

Infrared results (*cf.* Fig. 6, Table 5)

Our results are in good agreement with those of Schmelz *et al.*[18]. The infrared spectrum of $BaC_2O_4 \cdot 0.5H_2O$ has the main characteristics of a compound without coordinated oxalate groups and can be distinguished from an oxalato complex in a normal manner[1].

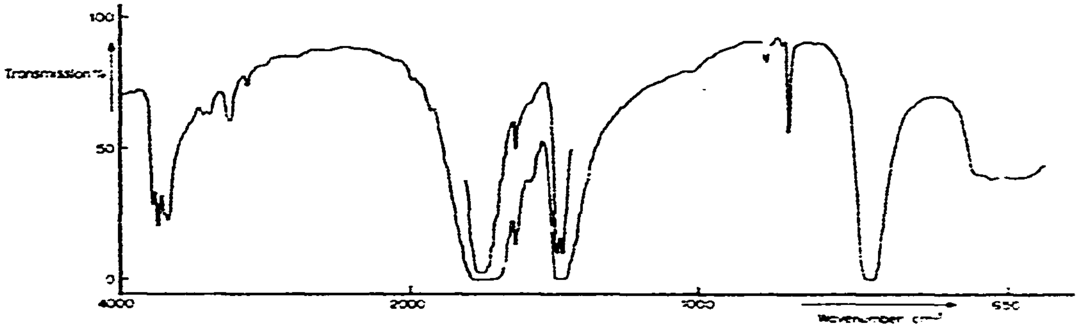

Fig. 6. Infrared absorption spectrum of $BaC_2O_4 \cdot 0.5H_2O$. Experimental conditions *cf.* ref. 1. Experimental results *cf.* Table 5.

TABLE 5

OBSERVED INFRARED WAVENUMBERS (cm^{-1}) OF $BaC_2O_4 \cdot 0.5H_2O$

BaC_2O_4 (ref. 17)	*$BaC_2O_4 \cdot H_2O$ (ref. 18)*	*$BaC_2O_4 \cdot 0.5H_2O$ (this work)*
		3600 sh
		3540 vs
	3500 m	3480 sh
	3400	3440 vs
		3115 w
		3060 w
		2905 m
		2780 w
	1620 vs	
	1600 vs	1605 sb
1530	1470 m	1470 m
	1325 vs	1324 vs
	1310 vs	1310 vs
1268		
1004		
894	896 w	897 w
860	866 m	865 s
767	771 vs	772 sb
672	662 m	<677 vb
650?		
	520 s	
	406 w	
	343 m	

vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, b = broad, vb = very broad.

DISCUSSION

In the oxalate decomposition two problems occur: the influence of the atmosphere on the decomposition mechanism and the elucidation of the different steps in this mechanism.

In a nitrogen atmosphere we observed a process with a lower procedural starting temperature (329°C) and a higher procedural final temperature (~550°C) than in the case of carbon dioxide (~410°C resp. ~530°C, Fig. 1). The larger weight loss rate in the first step is demonstrated by a decreasing slope in the transition range of the TG thermogram from 471°C on. A secondary reaction, separate from the earlier process is detectable in the TG thermogram at increased temperature (596–725°C). DTA and DSC thermograms show respectively two and one peak in a temperature range comparable with that of the two overlapping steps (DTA: 506°C, 526°C; DSC: 515°C). The secondary reaction is not detectable by DTA as a consequence of its low velocity, the involved amount of material and the properties of the enthalpimetric methods. $BaCO_3$ and an other phase were formed at 343°C, the latter vanishing at 391°C, as was demonstrated by our HTX results.

In carbon dioxide atmosphere TG shows a regular weight loss, no overlapping steps, no secondary reaction; DTA and DSC again show two peak patterns, shifted to higher temperature and broader than in the case of nitrogen (DTA: 537°C, 561°C; DSC: 539°C, 572°C). The HTX results gave the expected dehydration and oxalate decomposition temperatures, but no phase transition was observed in the 400°C range.

The oxalate decomposition is accompanied by carbon formation in nitrogen atmosphere at higher temperatures. It is followed by a secondary carbon/carbonate reaction. This proposed mechanism is in agreement with all experimental facts mentioned. The suppositions of intermediate oxalatocarbonates[6] and a phase transition in BaC_2O_4[2] are very improbable in view of the experimental conditions, applied by the relevant authors (air). The thermal behaviour of $BaCO_3$ is primarily dependent on the atmospheric conditions. Very low CO_2 partial pressure gives a solid state decomposition, the kinetic pattern of which is determined by the lattice type of the decomposing material. Atmospheric CO_2 pressure leads to a decomposition mainly occurring in the molten phase, temporarily strongly accelerated during the onset of melting. The procedural starting temperature of the $BaCO_3$ decomposition at 1 atm. CO_2 pressure is found to be 1348°C *i.e.* ~160°C lower than reported elsewhere[9].

CONCLUSION

The infrared spectrum and the thermal behaviour of $BaC_2O_4 \cdot 0.5H_2O$ make this compound suitable as a reference material for the study of the thermal decomposition of barium trioxalatoaluminate, synthesized by the authors*.

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*To be published.

The infrared spectrum has the normal characteristics of an ionic oxalate and can be used as a means for distinguishing this compound from a possible complex oxalate and/or carbonate in a manner already reported in literature[1]. Among the thermal behaviour data reported, those related to the dehydration are less important for the purpose mentioned above.

The thermal decomposition of the anhydrous compound is strongly dependent on the atmospheric conditions applied, which gives us a tool to change the mechanism and to shift the characteristic temperature ranges.

In a nitrogen atmosphere, poor in carbon dioxide, the oxalate decomposition starts with evolution of carbon monoxide. At higher temperature it is accompanied by the disproportionation of CO. A secondary reaction between $BaCO_3$ and C, takes place in a distinct temperature range.

$$BaC_2O_4\,(s) \rightarrow BaCO_3\,(s) + CO\,(g) \qquad (330\text{–}550\,°C)$$

$$2CO\,(g) \rightarrow C\,(s) + CO_2\,(g) \qquad (470\text{–}550\,°C)$$

$$BaCO_3\,(s) + C\,(s) \rightarrow BaO\,(s) + 2CO\,(g) \qquad (595\text{–}725\,°C)$$

$BaCO_3$ shows a decomposition in the solid state, fully finished before the possible eutectic melting of $BaCO_3$ and its decomposition product BaO (eutectic point: 1060 °C, 0.0661 atm., 64 mol % $BaCO_3$[14]).

$$BaCO_3\,(s) \rightarrow BaO\,(s) + CO_2\,(g) \qquad (703\text{–}1059\,°C)$$

In carbon dioxide atmosphere the decomposition of BaC_2O_4 in thin layers only shows the evolution of CO. The carbon formation and therefore the secondary reaction C/$BaCO_3$ is suppressed.

$$BaC_2O_4\,(s) \rightarrow BaCO_3\,(s) + CO\,(g) \qquad (410\text{–}550\,°C)$$

The decomposition of $BaCO_3$ is, after a small onset in the solid state, strongly accelerated during the initial melting and shows afterwards a less rapid evolution of carbon dioxide from the melt saturated with solid $BaCO_3$.

$$BaCO_3\,(s) \rightarrow BaO\,(s) + CO_2\,(g) \qquad (1325\text{–}1350\,°C)$$

$$(BaCO_3, BaO)\,(s) \rightarrow BaCO_3\,(s) + (BaCO_3 \cdot BaO)(l) \qquad (1350\text{–}1364\,°C,\ \text{rapid } CO_2 \text{ evolution}).$$

$$BaCO_3\,(s) \rightarrow (BaCO_3, BaO)(l) \qquad (1364\text{–}\ldots\,°C,\ \text{less rapid } CO_2 \text{ evolution}).$$

A 3 to 1 molecular mixture of $BaCO_3/\alpha\text{-}Al_2O_3$ shows in nitrogen atmosphere a thermogravimetric pattern, not distinguishable from the decomposition of pure $BaCO_3$. On the contrary in comparison with pure $BaCO_3$ in carbon dioxide atmosphere the temperature range of CO_2 evolution is shifted to much lower temperatures. This solid state reaction between $BaCO_3$ and $\alpha\text{-}Al_2O_3$ shows a change in kinetic pattern at the phase transition of $BaCO_3$. These phase transitions are already known from literature[9]; they are confirmed by DTA measurements in this contribution.

A phase transition in anhydrous BaC_2O_4[2] and the occurrence of intermediate oxalatocarbonates[6] in the first step of its decomposition, could not be confirmed in this study. The results of the other thermal analysis techniques applied, are in reasonable agreement with the proposed decomposition, mainly based on TG measurements.

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