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In celebration of the 60th birthday of Dr. Andrew K. Galwey

KINETICS AND MECHANISM OF THE THERMAL DECOMPOSITION OF BARIUM TITANYL OXALATE

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Abstract

Thermal analysis of barium titanyl oxalate reveals that the decomposition proceeds through four distinct rate processes. Among them, the decomposition of oxalate occurs in the temperature range 230–350°C, and has been studied by TG and gas pressure measurements, supplemented by IR spectroscopy, electron microscopy and chemical analysis. Oxalate decomposition proceeds differently in vacuum and in flowing gas atmospheres. Analytical results indicate the formation of a complex carbonate together with CO, CO_2 and water vapour below 400°C. Schemes for each type of decomposition are proposed and discussed. For decomposition in vacuum, kinetic observations fitted the three-dimensional, diffusion controlled, rate equation for almost the entire α-range ($0.028 \leq \alpha \leq 0.92$). The activation energy is calculated to be3 189±6 $kJ \cdot mol^{-1}$.

Keywords: barium titanyl oxalate, kinetics, mechanism of thermal decomposition, solid state decomposition, TG

Introduction

In continuation of our earlier work [1–3], the present study deals with the thermal decomposition of barium titanyl oxalate tetrahydrate (BTO). Since metal titanates have interesting electrical properties that are strongly influenced by the temperature of calcination [4, 5], a systematic kinetic study has been made of the thermal reaction of BTO leading to the formation of barium titanate. In spite of many investigations [4, 8], little information [8] is available on the kinetics of the multistage decomposition of BTO. Based on the thermoanalytical and X-ray diffraction studies [4–8], several schemes for the decomposition of BTO have been proposed. These can be broadly summarised as (i) dehydration followed by, (ii) decomposition of the anhydrous oxalate to the carbonate and finally (iii) the carbonate decomposition with formation of the

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metal titanates. The present paper reports a kinetic and mechanistic study of the second stage, the oxalate decomposition.

Experimental

Barium titanyl oxalate tetrahydrate was prepared by the method of Claubaugh *et al.* [9]. Experimental conditions were slightly altered [10] (4N HCl, 65°C) to obtain a product with a Ba:Ti ratio close to stoichiometry. Analysis [11] of the prepared reactant salt gives the composition as $BaTiO(CO_4)_2 \cdot 4H_2O$ with Ti content slightly greater than that of Ba (Ba:Ti = 1:1.026).

The kinetics of the thermal decomposition were studied in the temperature range 236–326°C using a conventional vacuum manifold with traps and calibrated dead space. A manually operated Mcleod gauge and Baratron diaphragm gauge were used. Output from the Baratron gauge was recorded [12] and values of pressure, time and temperature were stored in a Sinclair spectrum microcomputer for further analysis [13]. The experimental runs in vacuum (10^{-5} mmHg) were extended up to a maximum of 1000 minutes, depending on temperature. As carbon monoxide, carbon dioxide and water vapour were the only gaseous products of decomposition, use of liquid nitrogen and acetone slurry traps enabled the pressures of CO alone and those of CO, CO_2 together to be recorded. The original and partially-decomposed samples were analysed by infrared spectrophotometry over the range 400–4000 cm^{-1}. The oxalate contents of partially-decomposed samples at various temperatures were estimated by titration with standard $KMnO_4$ solution. Thermogravimetry (TG) in flowing atmosphere of air and nitrogen in the temperature range 30–700°C was also used. The structures of BTO samples after thermal treatment (5 hrs) at different temperatures ranging from 200–700°C were identified by XRD using Ni-filtered CuK_α radiation. Scanning electron microscopic examinations of the textures of the original and partially-decomposed samples were carried out with a Jeol 35 CF instrument. To study the effect of irradiation, samples in glass ampoules were irradiated with ^{60}Co γ-rays to a total dose of 2.5×10^8 Rad.

Results

Thermogravimetry

Thermal analysis of BTO by thermogravimetry in the temperature range 30–700°C shows that decomposition occurs in several steps. The TG curves in air and in nitrogen are almost identical. Typical results from such a study are

Table 1 Results from TG studies

Atmosphere	Mode of measurement	Peak	Temperature / °C	Mass loss / % (approx.)
Air	165 deg·min^{-1}	(i)	170	≈16
	20 mm/min	(ii)	252	≈6.5
	30–700°C	(iii)	350	≈16
		(iv)	595	Negligible
		(v)	695	≈9.8
Nitrogen	165 deg·min^{-1}	(i)	178	≈15.5
	20 mm/min	(ii)	250	≈6.2
	30–700°C	(iii)	350	≈16
		(iv)	600	Negligible
		(v)	702	≈9.5
Air	20 deg·min^{-1}	(i)	100–190	≈15.8
	20 mm/min	(ii)	210–278	≈6.5
	30–400°C	(iii)	280–370	≈16
Nitrogen	20 deg·min^{-1}	(i)	100–185	≈15.5
	20 mm/min	(ii)	190–270	≈6.2
	30–400°C	(iii)	270–370	≈16

presented in Table 1. The final mass loss is about 48% with peaks for the DTG curves at ≈170, 250, 350 and 700°C. The corresponding mass losses are about 15–16, 6.5, 16 and 9.5% respectively. Since CO, CO_2 and H_2O are the only gaseous products of decomposition, the mass losses correspond, respectively, to the loss of four molecules of H_2O, one molecule of CO, one molecule each of CO and CO_2 and finally one molecule of CO_2. Thus, from the TG studies, the decomposition below 400°C can be represented as

$$BaTiO(C_2O_4)_2 4H_2O \rightarrow \text{solid products} + 2CO + CO_2 + 4H_2O \qquad (1)$$

Infrared analysis

Infrared spectra were obtained for samples of barium titanyl oxalate decomposed at various selected temperatures to different extents. For undecomposed

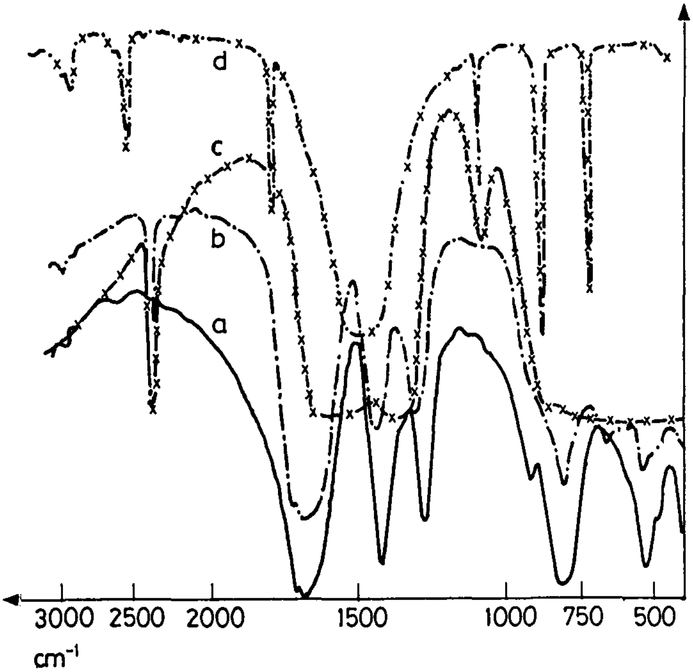

Fig. 1 IR spectra of (a) undecomposed BTO, (b) BTO heated at 300°C in vacuum till $d\alpha/dt$ first reaches a minimum, (c) heated at 355°C for 6 hours ($\alpha \approx 1$), (d) $BaCO_3$ (BDH)

BTO (Fig. 1a), the principal band of oxalate (ν_{as}, C=O) occurs at 1686 cm^{-1}. This maximum shifts to 1678 cm^{-1} (Fig. 1b), for the sample heated up to the end of initial rapid reaction at 300°C in vacuum, i.e., when the rate of decomposition first reaches the minimum value (after about 12 min at 300°C). In addition to the shift of about 8 cm^{-1} for the C=O frequency, a notable feature of Fig. 1b is the appearance of an intense band at 2339 cm^{-1} that can be attributed to the asymmetric stretching frequency of free CO_2. Disappearance of the small band at 912 cm^{-1} for the C–C stretching [14] is also noteworthy, as it is evidence that C–C bond rupture is probably the first stage of thermal breakdown of the oxalate anion [15]. The IR spectrum of BTO heated at 355°C in vacuum for 6 hours ($\alpha = 1$) is presented in Fig. 1c. The intense band at 2339 cm^{-1} is unchanged, but the ν_{as}, C=O band at 1686 cm^{-1} loses symmetry, shifts to 1617 cm^{-1} and almost overlaps with the band at 1358 cm^{-1}. The entire combination bears resemblance to the principal band of carbonate at 1450 cm^{-1}

(Fig. 1d). The band at 1056 cm^{-1} and the weakly active bands at 846 cm^{-1} and 657 cm^{-1}, characteristic of carbonates [16] (compare Fig. 1d) are noteworthy. The absence of any peak in the 1800–2200 cm^{-1} region for all the spectra excludes the presence of any co-ordinated carbonyl group or trapped carbon monoxide. The overall information from the IR spectra may thus be summarised as (i) the reaction is initiated with the rupture of C–C bond of the oxalate group (ii) CO_2 is evolved in the initial stage of decomposition in vacuum and (iii) although carbonate is most likely the final product of decomposition below 400°C, the product is possibly not a simple carbonate.

X-ray diffraction

X-ray diffraction analyses of BTO samples after being heated (5 hrs) at different temperatures ranging from 200–700°C indicate no notable feature below 500°C. Clearly BTO breaks down upon dehydration below 200°C. At 500°C, very small peaks for the (111) plane of $BaCO_3$ and TiO_2 appeared. With further rise in temperature the (110) and (111) planes of $BaTiO_3$ appear, with a corresponding decrease in the peaks for $BaCO_3$ and TiO_2. In agreement with the IR data, these observations ruled out formation of any barium oxalate in the temperature range of study (236–326°C). Formation of separate $BaCO_3$ and TiO_2 phases may be possible after heating at 500°C.

SEM studies

Electron microscopy studies revealed no evidence of melting or sintering during decomposition. Typical reactant crystallites (Fig. 2a, $\alpha = 0$) were usu-

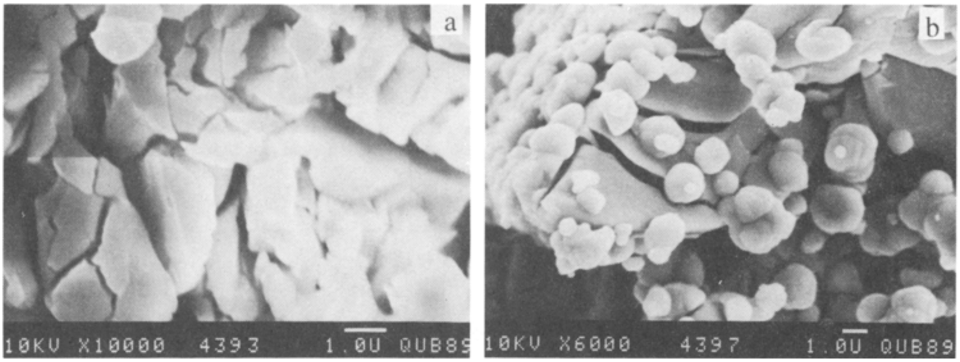

Fig. 2 Electron micrographs of BTO (a) undecomposed, (b) $\alpha = 0.3$ at 322°C

ally $1–2\times10^{-9}$m with approximately planar surfaces. Some aggregates of crystallites have rounded surfaces. Thermal treatment results in the appearance of globular particles (Fig. 2b, 322°C, $\alpha = 0.3$) covering almost the entire surface of the crystallites. The final product is pseudomorphic with the undecomposed reactant crystallite.

Gas pressure measurement

About 30 mg of the dehydrated salt (80°C, 2 h), accurately weighed, was used in each experimental run to study the thermal decomposition of BTO in the temperature range 236–326°C. The pressures (P) measured at suitable time intervals were recorded until achievement of a final pressure value (P_f), that remained unaltered for one hour. Figure 3 shows representative plots of fractional decomposition $\alpha(=P/P_f)$ *vs.* time at different temperatures. These pressures were recorded using a liquid nitrogen trap (78 K) and hence correspond to the pressures of CO only. The decomposition curves are deceleratory throughout and are highly reproducible. Each such curve is characterised by an initial rapid evolution of gas followed by a long decay period. The reduced-time plots i.e.,

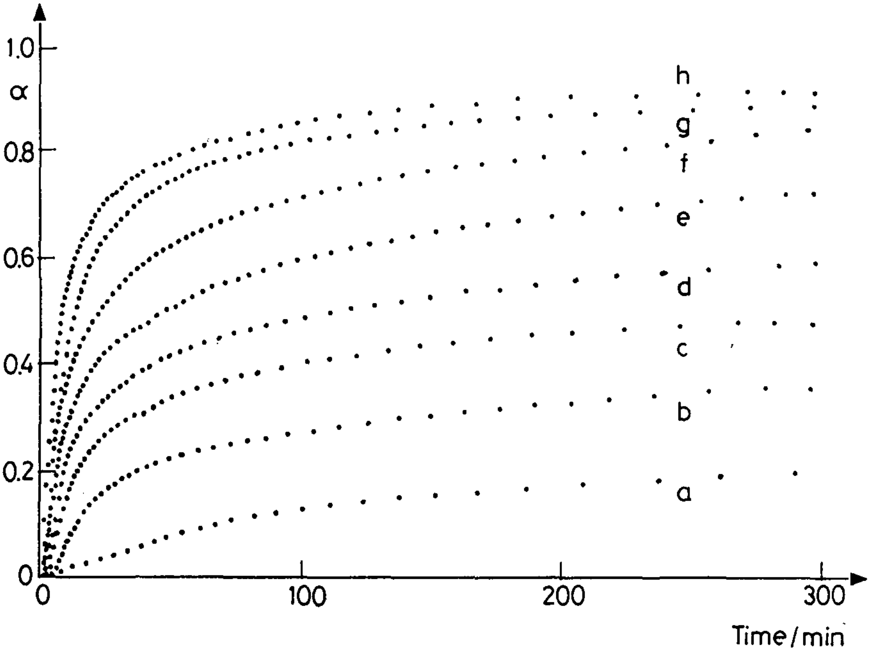

Fig. 3 α–t plots for oxalate decomposition: a-241, b-261, c-280, d-289, e-301, f-310, g-321 and h-326°C

α *vs.* $t/t_{0.5}$, for reactions within this temperature interval are almost superimposable. From this similarity of kinetic characteristics, it is concluded that the mechanism of decomposition is essentially the same over the temperature range studied.

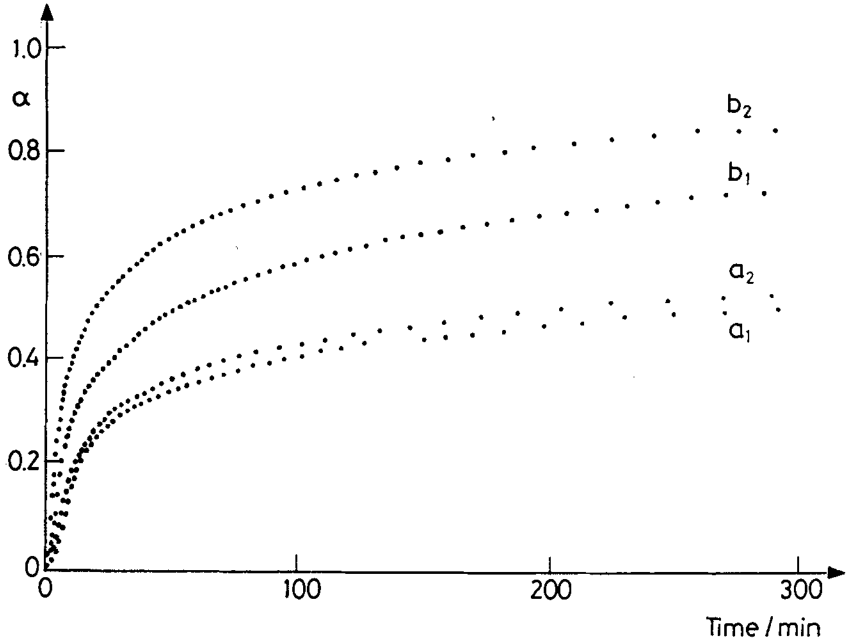

Fig. 4 α–t plots from CO_2 and CO pressure measurements: a_1 and a_2 refer respectively to CO_2 and CO pressure at 280°C while b_1 and b_2 refer to the pressure values at 310°C

The characteristic features of the α–t plots for CO_2 evolution are remarkably similar to those for CO evolution (Fig. 4). The curves are superimposable up to $\alpha = 0.3$. Over the decay stage ($\alpha > 0.3$) deviation is observed, with the rate of CO evolution being slower. Thus, during the early stages of decomposition, both CO and CO_2 are formed almost simultaneously by the same chemical process. From the plot of $d\alpha/dt$ *vs.* α (Fig. 5), where α corresponds to the CO pressure alone, the initial rapid evolution of gases increases with the increase in temperature, but maintains almost a constant ratio to the total decomposition ($\alpha = 0.12$) irrespective of temperature. At $(d\alpha/dt)_{max}$, the ratio of the partial pressures of CO to CO_2 is 1:1. The ratio remains almost constant for lengths of time which are dependent on temperature and the ratio then increases to a value of ~1.2 in the decay stage.

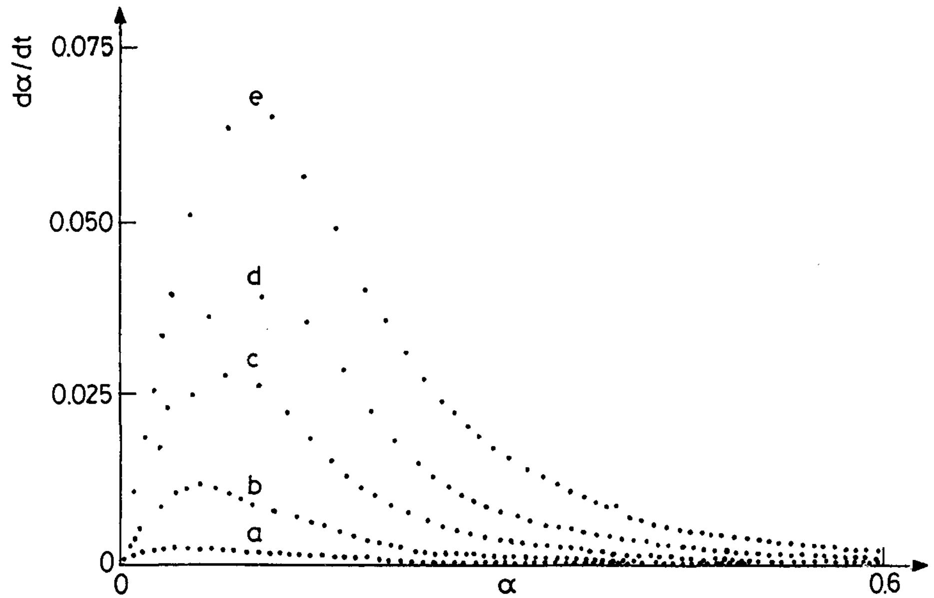

Fig. 5 dα/d*t* *vs*. α: a-241, b-261, c-280, d-289, e-301°C

There is a contradiction between the results of the isothermal studies in vacuum and those of TG measurements. Isothermal decomposition in vacuum gives clear indication of evolution of both CO and CO_2 in equimolecular proportions in the initial stages ($\alpha \leq 0.3$), followed by evolution of possibly one more molecule of CO. This is in contrast to the formation of one molecule of CO followed by one molecule each of CO and CO_2 proposed from TG studies. Similar observations have been reported earlier [15, 17] for the decompositions of simple oxalates and are explained as due to the reversal of the decomposition process in presence of accumulated CO.

Table 2 records the pressures of CO only (P_1), and those of CO + CO_2(P_2) for decomposition at temperatures throughout the interval of the present studies. After recording the P_1 values at the end of an experiment, the liquid N_2 trap was replaced by an acetone slurry trap to record the total pressure P_2. The Table also includes the corresponding pressures expected (P_{1E} and P_{2E}) supposing the decomposition reaction to proceed as per Eq. (2).

$$BaTiO(C_2O_4)_2 4H_2O \rightarrow BaTiO_2CO_3 + 2CO + CO_2 + 4H_2O \qquad (2)$$

A noteworthy feature of Table 2 is the constancy in the value of P_1/P_2 ratio over the entire temperature range studied. However, the high pressure of CO_2 at the end of a reaction is striking (P_1/P_2 value is 0.54 instead of 0.66 as per Eq. (2)). All residues of decomposition in vacuum or in nitrogen atmosphere are homogeneously brownish-black and the presence of elemental carbon has been confirmed. In air, however, the residues are uniformly white with no trace of residual carbon found.

The higher partial pressure of carbon dioxide may have resulted either from the reduction of titanium [18] (Eqs (3) and (4)) or through disproportionation of carbon monoxide to carbon dioxide.

$$2BaTiO(C_2O_4)_2 4H_2O \rightarrow Ba_2Ti_2O_2(C_2O_4)_3 + 2CO_2 + 4H_2O \qquad (3)$$

$$Ba_2Ti_2O_2(C_2O_4)_3 \rightarrow Ba_2Ti_2O_3(CO_3)_2 + 3CO + CO_2 \qquad (4)$$

The reaction involving reduction of titanium to the trivalent state, followed by oxalate decomposition, cannot be the explanation since it contradicts many experimental observations. The homogeneous brown colour of all residues suggests the disproportionation of CO to CO_2 as the possible cause

$$2CO \rightleftarrows CO_2 + C \qquad (5)$$

This explanation is further supported by the gradually increasing difference in calculated and observed total pressure values with rise in temperature, because CO disproportionation involves reduction of pressure to 50 percent of that given by CO alone. The deviations observed at high temperatures (Table 2) are probably due to a small amount of carbonate decomposition which increases the CO_2 pressure and disturbs the equilibrium in Eq. (5).

Based on the above evidence, the stoichiometric equation for oxalate decomposition is expressed as:

$$BaTiO(C_2O_4)_2 4H_2O \rightarrow BaTiO_2CO_3 + 1.496CO + 1.253CO_2 + $$
$$+ C_{0.251} + 4H_2O \qquad (6)$$

Using this stoichiometry, the combined pressure values for CO and CO_2 (P_c) at each temperature have been calculated (Table 2). The near perfect agreement of the observed and calculated pressure values supports the stoichiometry.

Kinetics of oxalate decomposition

The oxalate decomposition of BTO is predominantly deceleratory (Fig. 3). Pre-crushing and pre-irradiation (^{60}Co γ-rays) have virtually no effect on the ki-

Table 2 Calculated and observed pressure values for CO and CO+CO$_2$ at different temperatures

Temperature / °C	Decomp. / %	Pressure values / torr				$R=P_1/P_2$	Calculated** total pressure
		Observed		Calculated*			
		CO P_1	CO+CO$_2$ P_2	CO P_{1E}	CO+CO2 P_{2E}		P_c
236	31.8	0.701	1.274	0.935	1.402	0.550	1.285
241	36.9	0.815	1.488	1.087	1.630	0.548	1.495
251.5	42.7	0.944	1.709	1.258	1.887	0.552	1.730
253	45.3	1.000	1.802	1.333	2.000	0.555	1.836
261	55.1	1.217	2.198	1.623	2.434	0.554	2.234
270	58.2	1.285	2.330	1.713	2.590	0.551	2.354
280	67.7	1.495	2.669	1.973	2.990	0.560	2.745
289	81.6	1.801	3.289	2.401	3.602	0.548	3.307
301	83.7	1.848	3.370	2.464	3.696	0.548	3.393
310	96.9	2.138	3.994	2.851	4.276	0.535	3.926
321	98.0	2.170	4.023	2.883	4.325	0.539	3.963
326	99.7	2.200	4.095	2.933	4.400	0.537	4.033
353	>100	2.266	4.288	–	–	0.527	–
378	>100	2.277	4.300	–	–	0.529	–

The pressure values calculated using *Eq. 2 and **Eq. 6

netics of decomposition. The measured data at each temperature conform to the Zuravlev equation [19]

$$[(1-\alpha)^{-1/3}-1]^2 = kt \tag{7}$$

as the most appropriate kinetic expression. The very satisfactory linear plots for Eq. (7) from the data in Fig. 3 are shown in Fig. 6. Using a magnified scale (3 times that of Fig. 6) the α-range of applicability is determined as $0.028 < \alpha < 0.92$. While the lower limit value is slightly altered, the value for the upper limit decreases with a decrease in temperature owing to incomplete decomposition (Table 3). The Arrhenius activation energy was calculated 189±6 kJ·mol^{-1} with $\ln(A/\text{dm}^3\ \text{mol}^{-1}\cdot\text{s}^{-1}) = 41.2$.

Discussion

Titanyl oxalate decomposes to titanium dioxide, carbon monoxide and carbon dioxide in the temperature range 250–300°C [14, 20] while the decomposi-

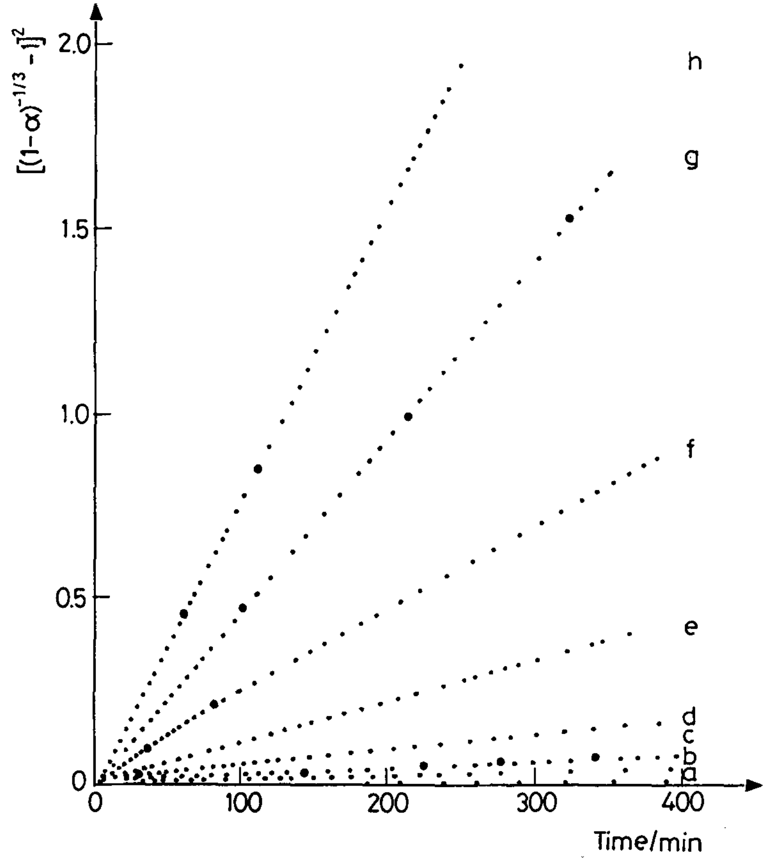

Fig. 6 Plot of $[(1-\alpha)^{-1/3}-1]^2$ *vs.* time: a-241, b-261, c-280, d-289, e-301, f-310, g-321 and h-326°C

tion of barium oxalate to carbonate and carbon monoxide occurs [21] at 400°C with an activation energy of 213 kJ/mol. BTO, on the other hand, undergoes 100% decomposition (Table 3) at 326°C with an activation energy of 189±6 kJ/mol.

Reaction mechanism

The primary question in proposing a mechanism for the decomposition of BTO is to ascertain (i) whether the decomposition of oxalate ion leads to one or two molecules of CO [6] and (ii) if CO and CO_2 are evolved simultaneously or in separate chemical processes. TG studies in flowing nitrogen or air yield posi-

Table 3 Results from kinetics of oxalate decomposition

Temperature / °C	Decomp. / %	α–range	k	Activation energy / kJ·mol^{-1}
241	36.9	0.1123–0.2468	$2.5641\cdot10^{-5}$	
261	55.1	0.0082–0.4150	$6.4103\cdot10^{-5}$	189±6
280	67.7	0.0159–0.5323	$1.8750\cdot10^{-4}$	
289	81.6	0.0145–0.6423	$3.8158\cdot10^{-4}$	ln(A / dm^3·mol^{-1}·s^{-1})
301	83.7	0.0314–0.7710	$1.0811\cdot10^{-3}$	
310	96.9	0.0150–0.8560	$2.2500\cdot10^{-3}$	41.2
321	98.0	0.0075–0.9113	$4.5800\cdot10^{-3}$	
326	99.7	0.1104–0.9125	$7.6900\cdot10^{-3}$	

tive information of only CO evolution in the initial stage, followed by evolution of both CO and CO_2, while these findings are reversed for studies in vacuum.

It has been pointed out that a reducible ion, Ti(IV) present, frequently undergoes reduction accompanied by the release of two molecules of carbon dioxide [22, 23]. The reduced cation is oxidised rapidly thereafter by the environment (CO_2) to form CO. Accordingly, Gallagher [6] suggested that one of the oxalate ions of BTO decomposes in the normal fashion to yield barium carbonate, whereas the other oxalate ion yields one molecule each of CO and CO_2 through an intermediate formation of short-lived Ti(II), Fang *et al.* [4] have proposed a similar mechanism based on the reduction of Ti(IV). However, this mechanism fails to explain the present observation for the evolution of CO alone in the TG studies of BTO. Rather the reversal of the steps observed for decomposition in vacuum leads to the possibility of an equilibrium process occurring in the initial stages of decomposition [15],

$$2CO_2^- \rightleftarrows COCO_3^{2-} \rightleftarrows CO_3^{2-} + CO \qquad (8)$$

The formation of carbonyl carbonate ion by isomerisation of the CO_2 radicals, which are formed by the rupture of C–C bond of one of the oxalate ions, generates CO in an equilibrium step. A flowing atmosphere facilitates this process, thus explaining the evolution of CO alone in the TG studies of BTO. However, for decomposition in vacuum, the accumulated CO pressure hinders the second equilibrium step. The carbonyl carbonate ion, being highly unstable, then decomposes in presence of the reducible ion (Ti(IV)) to form one molecule each of CO and CO_2 (Eqs (9) and (10)).

$$COCO_3^{2-} \rightarrow 2CO_2 + 2e^- \tag{9}$$

$$TiO^{2+} + CO_2 + 2e^- \rightarrow TiO_2 + CO \tag{10}$$

The second oxalate ion decomposes subsequently to form a mixed carbonate and CO. This mechanism for the decomposition of BTO is in agreement with all the experimental observations. Thus, in vacuum, the chemical processes leading to the decomposition of BTO can be represented as:

$$BaTiO(C_2O_4)_2 4H_2O \rightarrow BaTiO(C_2O_4)_2 + 4H_2O \tag{11}$$

$$BaTiO(C_2O_4)_2 \rightarrow BaTiO_2(C_2O_4) + CO + CO_2 \tag{12}$$

$$BaTiO_2(C_2O_4) \rightarrow BaTiO_2CO_3 + CO \tag{13}$$

Although there is uncertainty regarding the extent of disproportionation, an assumption of 50% disproportionation of total CO formed agrees remarkably well with the observed final partial pressures of CO and CO_2 as presented earlier.

In flowing atmosphere, however, after the initial dehydration, the decomposition proceeds through the following steps:

$$BaTiO(C_2O_4)_2 \rightarrow BaTiO(C_2O_4)CO_3 + CO \tag{14}$$

$$BaTiO(C_2O_4)CO_3 \rightarrow BaTiO_2CO_3 + CO + CO_2 \tag{15}$$

Formation of a mixed oxalate-carbonate with no definite stoichiometry has been proposed [8] for the initial stages of decomposition. The final product of decomposition below 400°C is $BaTiO_2CO_3$. This, as well as $BaTiO_2(C_2O_4)$, invariably contain trapped CO_2 responsible for the 2339 cm^{-1} band in the IR spectra of the decomposed sample.

Thermal decomposition of a solid may be considered as a two-step event consisting of (i) the thermal dissociation of the reactant molecules to form gaseous products and (ii) release of the latter to the outer surface [24]. If the reaction domain is considered compact, the pressure of accumulated gases has to reach some critical value before being released. The ease with which th gaseous products escape will thus depend on factors like the size of the domain, the concentration of the defects etc. However, for finely grained anhydrous BTO, the domains being very small, thermal dissociation and escape of gases will occur simultaneously. Observations like the absence of an induction period and the lack of influence on the reaction rate of pre-crushing and pre-irradiation, suggest that the oxalate decomposition of BTO belongs to the class where the reaction is rapidly initiated all over the surface. This in turn leads to sudden release of gaseous products and explains the fast initial stage of decomposition. The sudden release of gaseous products forms numerous pores and cracks in the bulk of the solid and the structure collapses closing or scattering the routes of gas escape. As the reaction continues, the gaseous products diffuse outward through the matrix. The rate gradually decreases with thermal densification of the matrix.

Conclusions

The oxalate decomposition of BTO can be summarised as follows:

The reaction is initiated by th rupture of one of the C–C bonds of the oxalate ion. The carbonyl carbonate anion formed in this way breaks in a reversible step to CO_3^{2-} releasing one molecule of CO. Flowing atmospheres favour this process. In vacuum, however, the second equilibrium step being hindered, the unstable carbonyl carbonate anion breaks down into one molecule each of CO and CO_2 in presence of Ti(IV).

Disproportionation of CO to CO_2 in the matrix results in lowering of $P_{CO}/P_{(CO+CO_2)}$ ratio. The stoichiometry for oxalate decomposition has been established from gas pressure measurements at various temperature as well as qualitative information from IR studies, oxalate estimation and XRD analysis. Carbon monoxide, carbon dioxide, water vapour and a complex carbonate are found to be the products of decomposition below 400°C.

For decomposition in vacuum, the α–t curves are deceleratory throughout and are almost similar for both CO and CO_2 evolution. In either case there is a rapid initial process due to instantaneous thermal reaction occurring all over the surface. This is followed by a prolonged, slow step attributed to the diffusion of trapped gaseous molecules through the gradually densifying matrix. The Zuravlev equation $[(1-\alpha)^{-1/3}-1]^2=kt$ describes the oxalate decomposition over almost the entire α-range.

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References

1 S. D. Bhattamisra and S. R. Mohanty, Rad. Effects, 29 (1976) 41.

2 S. D. Bhattamisra and S. R. Mohanty, J. Inorg. Nucl. Chem., 39 (1977) 2103.

3 S. D. Bhattamisra, G. M. Loverty, N. A. Baranov, V. B. Okhotnikov and A. K. Galwey, Phil. Trans. Roy. Soc. London A, 341 (1992) 479.

4 T.-T. Fang, H.-B. Lin and J.-B. Hwang, J. Am. Ceram. Soc., 73 (1990) 3363.

5 S. Rimlinger, L. Eyrand, P. Eyrand, J. C. Droguet and A. Beauger, Bull. Soc. Chim. Fr., 3 (1988) 432.

6 P. K. Gallagher and J. Thompson, Jr., J. Am. Ceram. Soc., 48 (1965) 644.

7 G. Pfaff, F. Schmidt, W. Ludwig and A. Feltz, J. Thermal Anal., 33 (1988) 771.

8 H. S. Gopalkrishnamurthy, M. S. Rao and T. R. N. Kutty, J. Inorg. Nucl. Chem., 37 (1975) 891 and the references there in from 1 to 3.

9 W. S. Clabaugh, E. M. Swiggerd and R. Gilchrist, J. Res. Nat. Bur. Std., 56 (1956) 289.

10 I. N. Belyaev and Yu. N. Orlyanskii, Russ. J. Inorg. Chem., 17 (1972) 589.

11 A. I. Vogel, Quantitative Inorganic Analysis, 3rd Ed., E. L. B. S., Longmans Green and Co., London 1961.

12 N. J. Carr and A. K. Galwey, Proc. Roy. Soc. London, A, 404 (1986) 101.

13 A. K. Galwey, P. J. Herley and M. A. A. Mohamed, J. Chem. Soc. Faraday Trans. I, 84 (1988) 729.

14 G. V. Jere and C. C. Patel, Indian J. Chem., 2 (1964) 383.

15 V. V. Boldyrev, I. S. Nev'yantser, Yu. I. Mikhailov and E. F. Khairetdinov, Kinetika i Kataliz, 2 (1970) 367.

16 T. S. Montgomery, J. Electrochem. Soc., 116(1969) 111.

17 O. Broadbent, D. Dollimore and J. Dollimore, J. Chem. Soc. A, (1966) 1491.

18 A. Glasner and M. Steinberg, J. Inorg. Nucl. Chem., 16 (1961) 279.

19 M. E. Brown, D. Dollimore and A. K. Galwey, Comprehensive Chemical Kinetics, Vol. 22: Reactions in the solid state, Elsevier, Amsterdam 1980, p. 70.

20 A. S. Bhatti and D. Dollimore, Thermochim. Acta, 79 (1984) 217.

21 D. Broadbent, D. Dollimore and J. Dollimore, Analyst, 94 (1969) 543.

22 P. K. Gallagher, Inorg. Chem., 4 (1965) 965.

23 A. Glasner, E. Levy and M. Steinberg, J. Inorg. Nucl. Chem., 25 (1963) 1415.

24 L. Stoch, Thermochim. Acta, 203 (1992) 259.

Zusammenfassung — Die Thermoanalyse von Bariumtitanyloxalat zeigte, daß die Zersetzung über vier Teilprozesse mit verschiedenen Geschwindigkeiten abläuft. Dabei verläuft die Zersetzung des Oxalates im Temperaturbereich 230-350°C, sie wurde mittels TG und Gasdruckmessungen untersucht, ergänzt durch IR-Spektroskopie, Elektronenmikroskopie und chemische Analyse. Die Oxalatzersetzung verläuft in Vakuum bzw. in strömenden Gasatmosphären verschieden ab. Die Analysenergebnisse zeigen die Bildung eines komplexen Karbonates zusammen mit CO, CO_2 und Wasserdampf unter 400°C. Für jeden Zersetzungstyp wurden Schemen vorgeschlagen und erörtert. Für die Zersetzung in Vakuum stimmten die kinetischen Beobachtungen mit der dreidimensionalen, diffusionskontrollierten Geschwindigkeitsgleichung für fast den gesamten α-Bereich ($0.028 \leq \alpha \leq 0.92$) überein. Die Aktivierungsenergie wurde mit einem Wert von 189±6 kJ/mol berechnet.