Journal of Thermal Analysis, Vol. 32 (1987) 1229–1241

THE IMPORTANCE OF THE CO_2^{2-} ANION IN THE MECHANISM OF THERMAL DECOMPOSITION OF OXALATES

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(Received January 13, 1986: in revised form December 16, 1986)

The effects of active (carbon dioxide and carbon monoxide) and neutral (helium, argon and nitrogen) atmospheres on the course of thermal decomposition of oxalates have been studied and compared. A mechanism of thermal decomposition has been proposed on the basis of the results obtained, the first stage of which consists in a heterolytic dissociation of the C—C bond, with the formation of carbon dioxide and the CO_2^{2-} anion.

In our earlier studies on the systematics of thermal decomposition mechanisms, it was shown that heterolytic cleavage is the first stage in the thermal decomposition of salts with bicentric anions containing a direct electron bond between the central atoms and a full coordination by oxide ligands (e.g. hyposulphates, $S_2O_6^{2-}$, and hypophosphates, $P_2O_6^{4-}$) [1, 2]:

$$S_2O_6^{2-} \rightarrow SO_3 + SO_3^{2-}$$

$$P_2O_6^{4-} \rightarrow PO_3^- + PO_3^{3-}$$

Since carbon is an element of the previous period, oxalates are analogues of hyposulphates and hypophosphates and in the first stage they should decompose analogously:

$$C_2O_4^{2-} \rightarrow CO_2 + CO_2^{2-}$$

Many radical [3–8] and ionic [9–20] mechanisms have been presented in the extensive literature on the thermal decomposition of oxalates. However, no one has considered the possibility of formation of the CO_2^{2-} anion, besides carbon dioxide, in the stage initiating the decomposition. The direct detection of the CO_2^{2-} anion in the progressing thermal decomposition is not possible at present. Due to this, indirect methods have been applied, consisting in a study and comparison of the influence of carbon monoxide and carbon dioxide atmospheres and of inert gases

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(helium, argon and nitrogen) on the thermal stability of oxalates. (An increase in the thermal stability of barium oxalate in a carbon dioxide atmosphere in comparison to that in nitrogen was reported in paper [21], but no interpretation of this fact was given.) The reaction of sodium hydroxide with sodium oxalate [22] and the thermal decomposition of potassium oxalate under vacuum [23] have also been considered. The possibility of the formation of the CO_2^{2-} anion besides carbon dioxide in the first stage of the thermal decomposition was justified in the intentionally limited cases of lithium, sodium, calcium and barium oxalates, where carbonates and carbon oxide were the main final products. The usefulness of the proposed mechanism for the interpretation of the thermal decomposition of oxalates yielding other products will be described later in this paper.

Experimental

Reactants

The following commercial reactants (p.a. POCh, Poland) were used: $Li_2C_2O_4 \cdot 2H_2O$, $Na_2C_2O_4 \cdot 2H_2O$, $CaC_2O_4 \cdot H_2O$, $BaC_2O_4 \cdot 0.5H_2O$ and $FeC_2O_4 \cdot 2H_2O$. The oxalates $MgC_2O_4 \cdot 2H_2O$, $ZnC_2O_4 \cdot 2H_2O$, $CdC_2O_4 \cdot 3H_2O$, SnC_2O_4, $Bi_2(C_2O_4)_3 \cdot 4H_2O$, $MnC_2O_4 \cdot 2H_2O$, $CoC_2O_4 \cdot 2H_2O$, $NiC_2O_4 \cdot 2H_2O$, CuC_2O_4, $La_2(C_2O_4)_3 \cdot 10H_2O$ and $Nd_2(C_2O_4)_3 \cdot 10H_2O$ were obtained from the respective chlorides (p.a. products of POCh, Poland, except for lanthanum and neodymium chlorides, which were p.a. products of BDH) and oxalic acid (p.a. POCh, Poland) or sodium oxalate. The anhydrous oxalates of mercury(I) and (II), lead (II) and silver were obtained from the respective nitrates (p.a. POCh, Poland) and oxalic acid. Anhydrous thallium(I) oxalate was precipitated by treating thallium(I) carbonate with oxalic acid; thallium(I) carbonate was obtained from the exchange reaction of barium carbonate (p.a. POCh, Poland) and thallium(I) sulphate (p.a. POCh, Poland).

Procedure

Simultaneous techniques of thermal analysis (TG, DTG and DTA) were carried out on an OD-202 derivatograph. The following temperatures characterizing the thermal decompositions of the compounds were measured within an accuracy of ± 2 deg: TG_i and TG_f = the initial and final temperatures of mass losses, DTG_p = temperature of the maximum reaction rate, and DTA_p = temperature of the maximum endo- or exothermic effects (the latter denoted by x).

Samples of salts containing one mmol of oxalate anion were placed in a platinum crucible (height 7 mm, diameter 8 mm). Experiments were carried out under a dynamic atmosphere of helium, argon, nitrogen, carbon monoxide or carbon dioxide (flow rate 100 ml/min). The heating rate was 6 deg/min. Alumina was used as inert reference material.

For the identification of substances in the solid phase, X-ray diffraction using Cu K_α rays was applied by means of a TUR–M–62 apparatus (GDR). Infrared spectroscopy was also applied, using a Specord–IR 75 spectrophotometer (GDR). For the identification of substances in the gas phase, infrared spectroscopy was applied as described below. Salts containing crystal water were dehydrated in a nitrogen stream in a tube furnace directly before the measurements of the gaseous products. The samples of gaseous products of thermal decomposition in a quartz tube furnace under a static nitrogen atmosphere were transported by a nitrogen stream directly from the furnace to a gas cell placed in the measuring chamber of the spectrophotometer.

Results and discussion

Data on the influence of the atmosphere on the thermal stabilities of chosen oxalates of alkali metals (Li^+ and Na^+) and alkaline earth metals (Ca^{2+} and Ba^{2+}) are given in Table 1. These results indicate analogous courses of thermal decomposition under particular experimental conditions. The lack of a significant effect of the nature of the atmosphere on the initial and final temperatures of the reactions was found in experiments carried out under inert gases (helium, argon and nitrogen) and carbon monoxide. The highest initial temperatures of mass losses and also the narrowest temperature ranges of the process were observed when the thermal decompositions of the oxalates were carried out under a carbon dioxide atmosphere. (Analogous data have been reported for the thermal decomposition of barium oxalate [21].) The solid products in all experiments were carbonates and elemental carbon. Elemental carbon results from the disproportionation of carbon monoxide: .

$$C_2O_4^{2-} \rightarrow CO_3^{2-} + CO$$

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

The amount of elemental carbon depends on the nature of the atmosphere used in the experiments, which is reflected in the recorded mass losses.

In an analysis of the influence of the atmosphere on the initial temperature of the reaction, the possibility of the limiting of the rate of thermal decomposition by effects connected with mass and heat transport should be taken into account. The diffusion and thermal conductivity coefficient are the parameters characterizing the

Table 1 Influence of the measuring atmosphere on the thermal decomposition course of lithium, sodium, calcium and barium oxalates

Counter-ion	Atmos-phere	TG_i °C	DTG_p °C	DTA_p °C	TG_f °C	Mass loss found, %	Mass loss calc., %	$\frac{CO}{CO+CO_2}$ % [a]
Li^+	He	448	513	515	530	25.0	27.46	52
	Ar	450	512	513	532	25.1	27.46	
	N_2	450	513	514	530	24.6	27.46	
	CO	450	516	520	537	22.7	27.46	
	CO_2	495	530	530	540	25.7	27.46	
Na^+	He	466	548	550	565	19.2	20.91	65
	Ar	463	550	552	566	18.9	20.91	
	N_2	465	550	552	565	19.1	20.91	
	CO	468	558	558	567	18.0	20.91	
	CO_2	503	558	560	568	19.6	20.91	
Ca^{2+}	He	369	436	442	486	22.4	21.87	94
	Ar	366	440	442	496	22.2	21.87	
	N_2	367	438	443	490	22.3	21.87	
	CO	370	447	449	496	21.5	21.87	
	CO_2	423	458	462	498	22.0	21.87	
Ba^{2+}	He	396	492	495	550	11.5	12.43	71
	Ar	400	494	497	550	11.5	12.43	
	N_2	398	494	496	548	11.5	12.43	
	CO	404	498	503	547	10.8	12.43	
	CO_2	463	508	510	550	12.0	12.43	

[a] estimated from IR spectroscopy measurement of gaseous product

mass and heat transport in this case. These coefficients depend on the temperature and on the nature of the atmosphere (approximately on its molar mass), as shown in the diagrams (Figs 1 and 2). From a comparison of the diffusion and thermal conductivity coefficients of the different gases used in the experiments, it appears that they are similar (at any temperature) for carbon dioxide, carbon monoxide, nitrogen and argon. Considerable differences are observed between argon and helium, however. The experimentally recorded initial temperatures of mass loss are similar when neutral atmospheres are used (helium, nitrogen and argon, where T_i varies within ± 5 deg), but considerable deviations occur for carbon dioxide (T_i rises by about 50 deg). This shows that the influence of the carbon dioxide atmosphere on the rise of the initial temperature of the mass loss does not stem only from the changes in the values of the diffusion and thermal conductivity

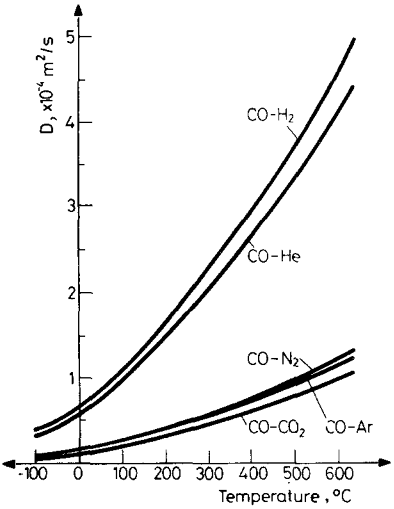

Fig. 1 Dependence of diffusion coefficients on the temperature for gases

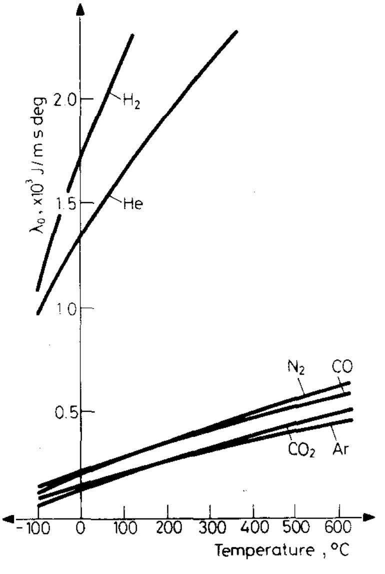

Fig. 2 Dependence of thermal conductivity on the temperature for gases

coefficients. This in turn indicates the reversibility of oxalate anion dissociation, which is shifted in favour of the substrate in the carbon dioxide atmosphere. On this basis it can be presumed that the first step, consisting in a heterolytic cleavage of the oxalate anion, limits the rate of thermal decomposition:

$$C_2O_4^{2-} \rightleftharpoons CO_2 + CO_2^{2-}$$

The lack of any effect of the presence of carbon monoxide indicates that this is formed is sufficient to promote the further decomposition of oxalate. This has the process.

The influence of oxygen, examined in most of the experimental studies on the thermal decomposition of oxalate, was explained by Dollimore and Griffiths [24]. The heat generated by the oxidation of the initial quantities of carbon monoxide formed in sufficient to promote the further decomposition of oxalate. This has the result that the temperature of decomposition in oxygen is either the same as in nitrogen, or a little lower, in spite of the increase in the carbon dioxide partial pressure.

The CO_2^{2-} anion is the second product, besides carbon dioxide, in the first stage. The major problem is the detection of this anion, or at least the fact that its existence is not excluded experimentally. It appears that compounds with such an anion (protonless formates: carbonites) can be obtained by treating carbon dioxide with metallic potassium besides the carbonate, carbon monoxide, carbon dioxide and compounds are thermally unstable and at ca. 100° undergo decomposition to yield the oxalate and the metal:

$$2\,Cs_2CO_2 \rightarrow Cs_2C_2O_4 + 2\,Cs$$

as well as the carbonate, carbon and carbon monoxide. The possibility of the existence of a CO_2^{2-} anion was justified theoretically by Walsh [26]. The presence of metallic potassium besides the carbonate, carbon imonoxide, carbon dioxide and elemental carbon in the products of thermal decomposition of potassium oxalate under vacuum [23] may be an indication of the advisability of considering the formation of the CO_2^{2-} anion in the thermal decomposition of oxalates. The formation of metallic potassium probably results from the formation of K_2CO_2 as an intermediate:

$$K_2C_2O_4 \rightarrow K_2CO_2 + CO_2$$

Carbon dioxide is removed from the reaction medium and K_2CO_2 decomposes to yield metallic potassium:

$$2\,K_2CO_2 \rightarrow K_2C_2O_4 + 2\,K$$

analogously as for Cs_2CO_2 [25].

Another indication confirming the formation of the CO_2^{2-} anion in the first stage of the thermal decomposition of oxalates is the similarity of the reaction products of sodium oxalate and sodium formate with sodium hydroxide. Both the oxalate and the formate undergo highly exothermic reactions with sodium hydroxide, in which sodium carbonate and hydrogen are the only products [22].

$$Na_2C_2O_4 + 2\,NaOH \rightarrow 2\,Na_2CO_3 + H_2 \tag{1}$$

$$HCO_2Na + NaOH \rightarrow Na_2CO_3 + H_2 \tag{2}$$

The results of these reactions can be interpreted as follows: the CO_2^{2-} anion is a strong proton acceptor and can occur as an intermediate only in an aprotic medium. In the presence of sodium hydroxide, however, it should be transformed to a formate anion:

$$Na_2C_2O_4 + NaOH \rightarrow HCO_2Na + Na_2CO_3$$

One of the products, sodium formate, cannot be isolated, due to the further reaction occurring in the alkaline medium (Eq. 2). The formation of identical products (sodium carbonate and hydrogen) in the two reactions (Eqs 1 and 2) indicates that the thermal decomposition of sodium oxalate in the presence of sodium hydroxide proceeds via an intermediate formate stage. This is in agreement with our postulate that the first stage in the thermal decomposition of alkali metal and alkaline earth metal oxalates involves the formation of carbon dioxide and the CO_2^{2-} anion.

It should be noted that under the conditions of thermal decomposition of oxalates the CO_2^{2-} anion does not form a stable phase, since it is a short-living intermediate. A kinetic equation can be derived on the basis of the quasistationary state method presented by Bodenstein for reactions in which the concentration of a short-living intermediate is very small. Due to the strong anion-donor properties of the CO_2^{2-} anion, it could be expected to undergo a direct acid-base reaction with carbon dioxide. The decomposition scheme could then be presented as follows: after the reversible first stage:

$$C_2O_4^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CO_2 + CO_2^{2-} \tag{3}$$

a reaction occurs between the products formed:

$$CO_2 + CO_2^{2-} \xrightarrow{k_2} CO_3^{2-} + CO$$

$$V_1 = k_1$$

$$V_{-1} = k_{-1}p_{CO_2}[CO_2^{2-}]$$

$$V_2 = k_2p_{CO_2}[CO_2^{2-}]$$

where:

k_1, k_{-1} and k_2 = the rate constants of the particular reactions,
p_{CO_2} = the actual pressure of carbon dioxide, and
$[CO_2^{2-}]$ = the concentration of the CO_2^{2-} anion, expressed as a fraction of the active surface [mol/m²].

The reversibility of the first stage will be noticeable for $k_1 > k_2$ or $k_{-1} \sim k_2$; from the stationary rule $\frac{d[CO_2^{2-}]}{dt} = 0$, we have

$$V_1 = V_{-1} + V_2$$

$$[CO_2^{2-}] = \frac{k_1}{p_{CO_2}(k_{-1}+k_2)}$$

The concentration of the CO_2^{2-} anion, $[CO_2^{2-}]$ as a fraction of the active surface, depends inversely on the pressure of carbon dioxide.

$$V_r = V_1 - V_{-1}$$

$$V_r = \frac{k_1 k_2}{k_{-1}+k_2}$$

From a study of the proposed scheme, it can be concluded that the rate of thermal decomposition of the oxalate, V_r, does not depend on the actual pressure of carbon dioxide, which is not in agreement with the experimental results.

In view of this it is necessary to consider a modified mechanism, assuming that after a reversible first stage (as previously) the dissociation of the CO_2^{2-} anion takes place in the presence of a counter-ion, but in the absence of carbon dioxide:

$$CO_2^{2-} \xrightarrow{k_2'} O^{2-} + CO \qquad (4)$$

The counter-ion is an acceptor of the oxide anion originating from the CO_2^{2-} anion dissociation:

$$O^{2-} + M^{2+} \rightarrow MO$$

Carbon dioxide reacts with a metal oxide with the formation of a carbonate (providing it is stable within the temperature range of the thermal decomposition of the oxalate):

$$MO + CO_2 \rightarrow MCO_3$$

The reaction rate of the second stage is expressed by

$$V_2' = k_2'[CO_2^{2-}]$$

When the conditions of the stationary rule for an intermediate are fulfilled:

$$V_1 = V_{-1} + V_2'$$

$$[CO_2^{2-}] = \frac{k_1}{k_{-1}p_{CO_2} + k_2'}$$

The concentration of the CO_2^{2-} anion as a fraction of the active surface decreases with increase of the actual concentration of carbon dioxide:

$$V_r = V_1 - V_{-1}$$

$$V_r = \frac{k_1 k_2'}{k_{-1}p_{CO_2} + k_2'} \tag{5}$$

Here, the rate of thermal decomposition of an oxalate, V_r, decreases with increase of the actual carbon dioxide pressure, which is in agreement with the experimental results. An influence of carbon dioxide on the rate of thermal decomposition of oxalates appears when

$$k_{-1}p_{CO_2} > k_2' \quad \text{or} \quad p_{CO_2}k_{-1} \sim k_2'$$

The rate of the thermal decomposition is then expressed by Eq. (5). In a particular case, when

$$k_{-1}\, p_{CO_2} \gg k_2'$$

expression (5) describing the rate of decomposition of an oxalate is simplified to

$$V_r = \frac{k_1 k_2'}{k_{-1}p_{CO_2}}$$

However, when the decomposition rate of the CO_2^{2-} anion increases markedly on increase of the temperature or on increase of the acidic properties of the counter-ion, so that

$$k_{-i}p_{CO_2} \ll k_2,$$

the rate of thermal decomposition of the oxalate will be less and less dependent on the actual pressure of carbon dioxide (Eq. 6), which is in agreement with the further course of the thermal decomposition:

$$V_r = k_1 \tag{6}$$

The thermal decomposition data relating to the oxalates of cations with considerable anion- or electronacceptor properties are given in Tables 2–4. It is noteworthy that, as concerns the oxalates studied, an effect of carbon dioxide on an

Table 2 Influence of the measuring atmosphere on the thermal decomposition course of lanthanum, neodymium and magnesium oxalates

Counter-ion	Atmosphere	TG_i °C	DTG_p °C	DTA_p °C	TG_f °C	Mass loss found, %	Mass loss calc., %	$\frac{CO}{CO+CO_2}$ % [a]
La^{3+}	N_2	383	425	428	466	31.1	31.75	39
	CO_2	424	453	456	515	24.2	23.62	
Nd^{3+}	N_2	368	419	421	458	31.7	31.13	44
	CO_2	411	440	442	492	25.4	23.15	
Mg^{2+}	N_2	332	482	486	514	62.8	64.11	47
	CO_2	385	453/473	459/479	513	63.9	64.11	

[a] estimated from IR spectroscopy measurement of gaseous product

Table 3 Thermal decomposition of oxalates with counter-ion revealing anion-acceptor and medium electron-acceptor properties

Counter-ion	TG_i °C	DTG_p °C	DTA_p °C	TG_f °C	Mass loss found, %	Mass loss calc., %	$\frac{CO}{CO+CO_2}$ % [a]
Sn^{2+}	300	358	360	380	35.5	34.83	48
Zn^{2+}	300	386	390	417	46.9	46.95	43
Mn^{2+}	350	414	419	434	51.0	50.37	47
Fe^{2+}	316	403	405	428	49.3	50.05	48

[a] estimated from IR spectroscopy measurement of gaseous product

increase of the thermal stability was only found for lanthanum, neodymium and magnesium oxalates (Table 2). This indicates that the mechanism of the first two stages (Eqs 3 and 4) of the thermal decomposition of these oxalates remains unchanged in comparison to that described previously for alkali metal and alkaline earth metal oxalates. The reversible character of the first stage and the lack of a noticeable influence of the acidic properties of the lanthanum, neodymium and magnesium cations on the rate of CO_2^{2-} anion dissociation are maintained. The oxide anions released in the dissociation of the CO_2^{2-} anion are bonded more strongly by cations with acidic properties, which causes a change in the nature of the final products. Instead of the carbonates obtained previously (Table 1), lanthanum and neodymium oxocarbonates are formed in nitrogen atmosphere:

$$La_2(C_2O_4)_3 \rightarrow (LaO)_2CO_3 + 2\,CO_2 + 3\,CO$$

Fig. 4 Thermal decomposition of oxalates with counter-ion revealing strong electron-acceptor properties

Counter-ion	TG_i °C	DTG_p °C	DTA_p^d °C	TG_f °C	Mass loss found, %	Mass loss calc., for		Solid product	M^a	CO^b
						oxide %	metal %		M+MO %	CO+CO_2 %
Cd^{2+}	286	383	388	406	43.2	35.93	43.91	Cd+CdO	91	4
Tl^{+}	312	326	330	376	17.6	14.49	17.72	Tl+Tl_2O	96	3
Pb^{2+}	300	358	360	380	27.6	24.39	29.81	Pb+PbO	60	29
Bi^{3+}	242	266	268	296	36.3	31.67	34.08	Bi+BiO	53	13
Co^{2+}	297	371	374	392	57.5	49.00	59.89	Co+CoO	85	13
Ni^{2+}	292	353	354	378	59.2	49.07	59.98	Ni+NiO	81	1
Cu^{2+}	232	256	255	265	57.6	52.79	58.07	Cu+Cu_2O	91	2
Ag^{+}	145	—^{c}	152	—^{c}	—^{c}	23.72	25.68	Ag	—	0.1
Hg_2^{2+}	129	158	160	173	19.2	14.75	17.99	Hg	100	0.3
Hg^{2+}	230	234	234	239	31.2	24.99	30.53	Hg	100	0.1

[a] the amount of metal was determined comparing the experimental mass loss values with those calculated for a metal oxide and metal.

[b] estimated from IR spectroscopy measurement of gaseous product.

[c] lack of data due to partial blowing out of the sample.

[d] exothermic effects marked with *x*.

and in carbon dioxide atmosphere:

$$La_2(C_2O_4)_3 \rightarrow La(LaO)(CO_3)_2 + CO_2 + 3\,CO$$

while the product of magnesium oxalate decomposition under both experimental conditions applied is the metal oxide:

$$MgC_2O_4 \rightarrow MgO + CO_2 + CO$$

The disproportionation of carbon monoxide takes place here only in the thermal decompositions of lanthanum and neodymium oxalates.

Not only anion-acceptor properties, but also electron-acceptor properties influence the nature of the final decomposition products of the oxalates of cations with high polarizabilities. Thus, a nonstoichiometric oxide with a higher content of metal (e.g. zinc, tin(II), manganese(II) and iron(II) oxalates; Table 3) may appear in the decomposition products [5], or a mixture of free metal and metal oxide (e.g. thallium(I), lead(II), cadmium, bismuth(III), cobalt(II), nickel(II) and copper(II) oxalates; Table 4) may be obtained. In the extreme case, when the electron-acceptor properties predominate considerably over the anion-acceptor ones (mercury(I) and

(II) and silver oxalates), the solid residue contains free metal and only traces of metal oxide, with a corresponding trace of carbon monoxide in the gaseous product (Table 4).

If the mechanism established previously is assumed, it can be expected that the redox reaction yielding free metal should disturb the reversible first stage of thermal decomposition, either by increasing the rate of oxalate anion cleavage (when the metal is the electron donor) or by retarding the reversible first-stage reaction leading to the formation of the oxalate anion (when the CO_2^{2-} anion is the electron donor). These processes may cause a lack of any noticeable influence of the carbon dioxide atmosphere on the thermal stabilities of the oxalates, irrespective of the type of redox reaction assumed, which is in agreement with the experimental results. Redox reactions may also cause the dissimilarity of the TG curves (autocatalytic type of decomposition) and decreases in the temperature ranges of thermal decomposition of the oxalates described here in comparison with the oxalates of alkali metals and alkaline earth metals. The conclusion obtained previously cannot be generalized, since with such clear differences in temperature the values of the kinetic parameters may be changed considerably.

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Zusammenfassung — Die Effekte von aktiven (Kohlendioxid und Kohlenmonoxid) und neutralen (Helium, Argon, Stickstoff) Atmosphären auf den Verlauf der thermischen Zersetzung von oxalaten wurden untersucht und miteinander verglichen. Aus den erhaltenen Ergebnissen wird ein Mechanismus der thermischen Zersetzung abgeleitet, dessen erster Schritt die heterolytische Dissoziation der C—C-Bindung unter Bildung von CO_2 und des CO_2^{2-}-Anions ist.

Резюме — Изучено и сопоставлено влияние активной атмосферы (моно- и двуокись углерода) и инертной (гелий, аргон и азот) на ход термического разложения оксалатов. На основании полученных результатов предложен механизм термического разложения, первая стадия которого вызвана гетеролитической диссоциацией связи C—C с образованием двуокиси азота и аниона CO_2^{2-}.