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FORMATION OF OXALATES AND CARBONATES IN THE THERMAL DECOMPOSITIONS OF ALKALI METAL FORMATES

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The influences of gaseous and solid reactants on the yields of oxalates and carbonates in the thermal decompositions of alkali metal formates have been studied. A mechanism of formation of these products is proposed, which explains the influences of basic and acidic species formed in the medium on the thermal decompositions of the alkali metal formates.

Extensive studies concerning the mode of thermal decomposition of alkali metal formates indicate a considerable effect of the process conditions on the yields of the main solid products, i.e. oxalates and carbonates formed according to the equations

$$2\,HCO_2^- \begin{array}{l} \nearrow H_2+C_2O_4^{2-} \qquad (1) \\ \searrow H_2+CO+CO_3^{2-} \qquad (2) \end{array}$$

The yield of oxalates was found to decrease in the following cation sequence: K^+, Na^+, Rb^+, Cs^+, Li^+ [1]. Oxalate formation is favoured by a higher reaction temperature range, and proceeds with a greater yield as the thermal stability of the oxalate increases [1–3]. The influence of the atmosphere on the oxalate yield has also been studied. Oxalate formation is retarded to a great extent in the presence of oxygen [1, 4, 5]. Similar oxalate yields are obtained in reactions under nitrogen and hydrogen atmospheres [1]. One hundred percent yields of the oxalate can be attained by carrying out the thermal decompositions of potassium and sodium formates in vacuum [5, 6]. An increase in the conversion of the formate to oxalate results from the addition of substances such as NaOH, $NaNH_2$, CH_3ONa, alkali metals and their amalgams [2, 3, 6–9]. The thermal decompositions of alkali metal formates have been explained by considering different variants of radical and ionic mechanisms [1, 5, 8, 10, 11]. However, the influence of the discussed parameters on the course of the process was usually considered selectively.

The reasons for the evolution of molecular hydrogen during the thermal

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decompositions of the alkali metal formates were described earlier [12, 13]. The further transformations of the carbon species resulting from hydrogen evolution (CO_2^{2-} anions and carbon dioxide), leading to the formation of oxalate and carbonate, are the subject of the present work.

The scheme proposed here for the thermal decomposition is in agreement with the literature results and our own experimental data. It also accords with the mechanism of thermal decomposition of oxalate presented in [14].

Experimental

Materials

Lithium, sodium and potassium hydroxides (p.a., POCh, Poland), sodium carbonate (p.a., POCh, Poland) and sodium borohydride (p.a., BDH) were used in the studies. The origins of the lithium, sodium and potassium formates were described previously [12].

Procedure

The thermal decompositions of the pure anhydrous substances and of their mixtures were carried out on an OD 202 derivatograph (MOM). Samples containing 2 millimoles of the formate were heated in a platinum crucible (diameter 8 mm, height 7 mm) under nitrogen, hydrogen, carbon oxide, carbon dioxide and oxygen atmospheres (flow rate 100 cm^3/min), at a heating rate of 6 deg/min, and in the case of sodium formate also at 3 deg/min and 1.5 deg/min. Alumina was used as a reference material. The amounts of oxalate and carbon in the solid residues were estimated from the TG curves and were confirmed by manganometric titration and gravimetric analysis, respectively.

The experimental results concerning the thermal decompositions of the formates, i.e. characteristic reaction temperatures—TG_i, DTG_p, DTA_p, TG_f (within an accuracy of ± 2 degrees), mass loss values suitable for determination of the ratio of products formed using the stoichiometric equations, and the yields of oxalate produced, are tabulated. The data on the further transformations of the other formate decomposition products, i.e. oxalates, which were reported in detail earlier [4], have been neglected here, as they did not give any additional information on the present problem: these steps proceed in sharply separated temperature ranges.

Results

The results of experiments carried out in the presence of compounds expected to show chemical activity towards decomposed formate were compared with those obtained for pure formate subjected to thermal decomposition in an inert gas (nitrogen) atmosphere.

The influences of the heating rate and the nature of the atmosphere used on the oxalate yields obtained from the thermal decompositions of lithium, sodium and potassium formates (Tables 1 and 2) were investigated. The yield of sodium oxalate was shown to decrease as the heating rate was lowered. Carbon oxide and hydrogen were found to behave like the inert gas (nitrogen), while carbon dioxide and oxygen strongly retarded sodium oxalate formation (Table 1). The analogous influence of carbon dioxide and oxygen in relation to an inert gas was confirmed with potassium formate (Table 2). No oxalate was found in the case of lithium formate in any of the reactions performed (Table 2).

Elemental carbon was found in the solid residues of formate decomposition carried out under a nitrogen atmosphere. The carbon amount corresponded to the disproportionation of 20–25% carbon oxide evolved during lithium formate decomposition. For the remaining formates, only traces of elemental carbon were

Table 1 Influence of the measuring atmosphere on the thermal decomposition of sodium formate

Atmosphere	TG_i, °C	DTG_p, °C	DTA_p^c, °C	TG_f, °C	Mass loss of Ist step, %	Oxalate yield in the 1st step product, %	Mass loss[d] of 2nd step, %
N_2	316	410	402 420x	438	15.2	33	22.0
N_2[a]	293	378	362 393x	410	17.5	23	22.1
N_2[b]	260	365	358 375x	385	18.0	19	22.0
H_2	318	390 414	414x	435	15.0	35	22.1
CO	318	415	400 418x	438	15.1	34	21.5
CO_2	318	412	412	440	21.1	6	22.2
O_2	285	385	387x	406	22.2	0	—

a) — heating rate 3 deg/min
b) — heating rate 1.5 deg/min
c) — exothermic effects marked with *x*
d) — second step is connected with thermal decomposition of sodium oxalate to sodium carbonate

Table 2 Influence of the measuring atmosphere on the thermal decomposition of lithium and potassium formates

Substrate	Atmosphere	TG$_i$, °C	DTG$_p$, °C	DTA$_p{}^a$, °C	TG$_f$, °C	Mass loss of Ist step, %	Oxalate yield in the Ist step product, %	Mass^b loss of 2nd step, %
HCO_2Li	N_2	304	383	390x	426	27.1	0	—
HCO_2Li	CO_2	300	377 396	387	424	27.3	0	—
HCO_2Li	O_2	280	380	382x	408	28.4	0	—
HCO_2K	N_2	328	428	413 435x	460	8.9	54	17.8
HCO_2K	CO_2	330	433	433	462	15.8	12	17.9
HCO_2K	O_2	294	410	413x	430	18.0	0	—

a) — exothermic effects marked with x

b) — second step is connected with thermal decomposition of potassium oxalate to potassium carbonate.

found. Carbon formation was diminished in a carbon dioxide atmosphere, and strongly reduced in the presence of oxygen.

The effects of sodium carbonate (Table 3), lithium, sodium and potassium hydroxides (Table 4) and sodium borohydride (Table 5) on the yields of the formate decomposition products were examined. The particular compounds were added in 5 mole % or equimolar amounts with respect to the formate. It should be stressed that the reactions with these reactants proceed in the liquid phase, since the studied

Table 3 Reaction of sodium formate with sodium carbonate in nitrogen atmosphere

Substrates	TG$_i$, °C	DTG$_p$, °C	DTA$_p{}^a$, °C	TG$_f$, °C	Mass loss of Ist step, %	Oxalate yield in Ist step product, %	Mass^b loss of 2nd step, %
$HCO_2Na+Na_2CO_3$ 1 :0.05	314	408	398 418x	435	13.8	34	20.1
$HCO_2Na+Na_2CO_3$ 1 : 1	298	396	385 403x	424	6.8	23	8.4

a) — exothermic effects marked with x

b) — second step is connected with thermal decomposition of sodium oxalate to sodium carbonate.

Table 4 Reactions of alkali metal formates with alkali metal hydroxides in nitrogen atmosphere

Substrates	TG_i, °C	DTG_p, °C	$DTA_p{}^a$, °C	TG_f, °C	Mass loss of Ist step, %	Oxalate yield in the Ist step product, %	Mass^b loss of 2nd step, %
$HCO_2Li + LiOH$ 1 : 0.05	270	356	338x 352 380x	390	25.8	0	—
$HCO_2Li + LiOH$ 1 : 1	236	250	238x^c	258	2.2	0	—
$HCO_2Na + NaOH$ 1 : 0.05	286	302	304x	318	0.9	92	20.1
$HCO_2Na + NaOH$ 1 : 1	212	—^{d}	212x^e	—^{d}	—^{d}	0	—
$HCO_2Na + LiOH$ 1 : 0.05	298	396	309x 342 410x	420	11.7	49	19.7
$HCO_2K + KOH$ 1 : 0.05	315	330	330x	350	2.7	93	16.3
$HCO_2K + KOH$ 1 : 1	225	—^{d}	225x^e	—^{d}	—^{d}	0	—

a) — exothermic effects marked with x

b) — second step is connected with thermal decomposition of sodium or potassium oxalate to corresponding carbonate

c) — initial temperature of the strong exothermic effect ($\Delta T = 15°$)

d) — lack of data caused by partial blowing away of sample in spite tenfold reduction of sample mass

e) — initial temperature of the strong exothermic effect ($\Delta T = 35°$)

formates undergo fusion before reaching the reaction temperature. Additionally, a significant lowering and contraction of the reaction temperature range was found in the reactions of all the formates with hydroxides and borohydride in comparison to that for the thermal decomposition of the pure formate. These effects were clearly intensified with increase of the amount of reactant added [3, 13].

The experimental results showed that addition of 5 mole % of the carbonate did not disturb the thermal decomposition of sodium formate. However, the addition of an equimolar amount of the carbonate with respect to the formate decreased the oxalate yield to 23% (Table 3).

The oxalate yields obtained from the formate-hydroxide reactions depended on the natures of the cations present in the reactants and on their mole ratio. An increase in the oxalate yield was observed for the thermal decompositions of mixtures containing sodium and potassium formates and a 5 mole % addition of

Table 5 Reaction of sodium formate with sodium borohydride in nitrogen atmosphere

Substrates	TG_i, °C	DTG_p, °C	$DTA_p{}^a$, °C	TG_f, °C	Mass loss of Ist step, %	Oxalate yield in Ist step product, %	Mass loss of 2nd step, %	Mass loss of 3rd step, %
HCO_2Na+ $+NaBH_4$ 1:0.05	264	292	295*x*	298	1.6	88	19.0[b]	—
HCO_2Na+ $+NaBH_4$ 1:1[c]	216	266	223*x* 250 270*x*	278	2.4	0	5.8	6.5

a) — exothermic effects marked with *x*

b) — second step is connected with thermal decomposition of sodium oxalate to sodium carbonate

c) — reaction of equimolar mixture is presented in paper [13].

the hydroxide of the same cation. However, no oxalates were found in the reaction products of an analogously prepared mixture of lithium formate and hydroxide. A small increase in the yield was obtained for the reaction of sodium formate with a 5 mole % addition of lithium hydroxide in comparison with that obtained for the decomposition of pure sodium formate. Only carbonates were found in the thermal decomposition products obtained from all the mixtures containing equimolar amounts of the formate and the hydroxide of the same cation, according to the equation

$$MOH+HCO_2M \rightarrow H_2+M_2CO_3 \quad (M = Li^+, Na^+, K^+) \tag{3}$$

The presence of 5 mol % of sodium borohydride affected the course of sodium formate decomposition in a similar way to sodium hydroxide, causing an increase in the oxalate yield from 33% to 88%. However, in the case of the reaction of an equimolar mixture of sodium borohydride and formate, described in [13], no sodium oxalate was found, but only sodium metaborate and various carbon compounds at low oxidation degrees, i.e. methane, carbon oxide, tar product and elemental carbon (Table 5).

Discussion

The reasons for the evolution of molecular hydrogen, which is the main gaseous product of thermal decomposition of the alkali metal formates, were described earlier [13]. Species with different stabilities (carbon dioxide and CO_2^{2-} anions) are formed as a consequence of hydrogen evolution:

$$2\,HCO_2^- \rightarrow H_2 + CO_2 + CO_2^{2-} \tag{4}$$

According to the considerations presented previously on the thermal decomposition of oxalate [14], CO_2^{2-} anions readily decompose to carbon oxide and oxide anions:

$$CO_2^{2-} \rightarrow O^{2-} + CO \tag{5}$$

The carbon dioxide generated in the first reaction step (Eq. 4) can subsequently react either with an oxide anion to produce a carbonate:

$$O^{2-} + CO_2 \rightarrow CO_3^{2-} \tag{6}$$

or with a short-lived CO_2^{2-} anion to produce an oxalate (providing this is thermally stable within the temperature range of thermal decomposition of the formate of the given cation):

$$CO_2^{2-} + CO_2 \rightleftharpoons C_2O_4^{2-} \tag{7}$$

The concentrations of carbon dioxide and CO_2^{2-} anions seem to have an essential effect on oxalate formation. A rise in the concentration of these species can be achieved by accelerating the process through an increase of the heating rate. A reverse result is obtained when the rate of temperature rise is lowered (Table 1) or when the system is diluted with sodium carbonate, which involves a decrease in the probability of oxalate formation, as revealed in the fall in its yield (Table 3).

The experimental results on the thermal decompositions of sodium and potassium formates in the presence of substances affecting the oxalate yield (carbon dioxide, sodium and potassium hydroxides and sodium borohydride) indicate the occurrence of acid-base reactions in the system. An increase of the concentration of basic species (hydroxide and hydride anions) (Tables 4 and 5) in the reaction medium favours oxalate formation, while the reverse effect is obtained when the concentration of acidic species (carbon dioxide) increases (Tables 1 and 2). The role of carbon dioxide is specific: its presence is essential for oxalate formation (Eq. 7) and, additionally, as the only acid in the reaction medium, carbon dioxide counteracts oxalate formation. Thus, an optimal carbon dioxide concentration exists, sufficient for it to act as a substrate in the reaction (Eq. 7), but at the same time low enough to minimize its action as an acid, which removes the basic species favouring oxalate formation from the system. A decrease in oxalate yield with respect to that of carbonate is observed for the thermal decompositions of sodium and potassium formates in a carbon dioxide atmosphere. However, the carbon dioxide pressure is minimal in thermal decompositions carried out under an inert gas flow (e.g. nitrogen), and the oxalate yield then increases. Under high vacuum conditions, part of the carbon dioxide formed according to Eq. (3) is removed, which causes an increase in the concentration of the basic species in the condensed phase. Hydrogen and the corresponding oxalate are the products of the thermal decompositions of sodium and potassium formates here [5, 6].

The explanation can be extended to the other gaseous atmospheres. An oxygen atmosphere causes the oxidation of carbon oxide formed in the decomposition. A considerable increase of the carbon dioxide partial pressure seems to be a sufficient reason for a retardation of the formation of sodium and potassium oxalates, despite their stability under these temperature conditions (Tables 1 and 2). The lack of influence of hydrogen and carbon oxide atmospheres on the oxalate yield confirms the hypothesis of the irreversible character of hydrogen evolution [13], and indicates that these gases do not take part in secondary reactions connected with the formation of oxalate and carbonate.

The addition of 5 mole % of sodium or potassium hydroxide to the formates of these cations causes a great increase in the oxalate yield (Table 4). Such an effect can not be explained merely by carbon dioxide bonding with the hydroxides; this would lead to a stoichiometric amount of the carbonate, which, as was proved experimentally (Table 3), does not disturb the thermal decomposition of the formate. This indicates that the action of hydroxides consists in the catalytic acceleration of the thermal decomposition of formate, according to the equations

$$OH^- + HCO_2^- \rightarrow O^{2-} + H_2 + CO_2 \tag{8}$$

$$O^{2-} + HCO_2^- \rightleftharpoons OH^- + CO_2^{2-} \tag{9}$$

From reaction 8 and 9, it appears that basic species (oxide or hydroxide anions) react directly with formate anions, causing increases in the concentrations of CO_2^{2-} anions and carbon dioxide, substrates essential for oxalate formation. Moreover, basic species are reproduced in the reaction system.

Our considerations on the course of the reaction between an equimolar mixture of sodium oxalate and sodium hydroxide, presented in [14], indicate that reaction 9 is reversible. This is consistent with the differentiation of the influence of the hydroxides examined on the oxalate yields obtained from the reactions with formates (Table 4). Lithium hydroxide binds the proton more weakly than sodium and potassium hydroxides do, which causes a shift to the left in the reaction equilibrium described by Eq. (9). Then, after reaction 8, reaction 9 stops, which promotes carbonate formation according to Eq. (6).

However, an increase of the hydroxide content in the mixture with formate (1 : 1) causes the consumption of formate in reaction 8, and consequently leads to carbonate formation according to Eq. (6).

The addition of 5 mole % of sodium borohydride (a hydride anion donor) leads to the transformation of formate anions to CO_2^{2-} anions. If it is assumed that the reaction proceeds via the $(BH_3CO_2)^{2-}$ adduct [15], stabilizing the CO_2^{2-} anions, oxalate formation in the presence of formate anion takes place according to the equations

$$BH_4^- + HCO_2^- \rightarrow H_2 + (BH_3CO_2)^{2-} \tag{10}$$

$$(BH_3CO_2)^{2-} + HCO_2^- \rightarrow BH_4^- + C_2O_4^{2-} \tag{11}$$

In the case of an equimolar mixture of sodium borohydride and formate, a lack of oxalate and carbonate is found in the reaction product (Table 5), which results from the quantitative transformation of formate anions to CO_2^{2-} anions according to Eq. (10) [13].

Analysis of the influences of strongly basic hydroxides and sodium borohydride on the oxalate yields shows that both reactants increase the rate of formate decomposition by facilitating the molecular hydrogen synproportionation in the hydride-proton mechanism. The qualitative and quantitative compositions of the products depend here only on the mole ratio of reactants used.

In the view of the mechanism proposed, the known effects of sodium amide [8] and sodium methanolate [7] concerning the increased yield of oxalate from the thermal decompositions of alkali metal formates seems to be analogous to the action of basic species, described previously. Due to its strong electron-donor properties, however, the action of metallic sodium [9] is probably initiated by an electron transfer, either directly to the formate anionic sublattice:

$$HCO_2^- \xrightarrow{\bar{e}} (HCO_2)^{2-} \begin{array}{ll} \nearrow H + CO_2^{2-} & \qquad (12) \\ \searrow H^- + CO_2^- & \qquad (13) \end{array}$$

or to the initially formed carbon dioxide:

$$CO_2 \begin{array}{ll} \xrightarrow{\bar{e}} CO_2^- & \qquad (14) \\ \xrightarrow{2\bar{e}} CO_2^{2-} & \qquad (15) \end{array}$$

In the presence of metallic sodium in the system, the concentration of CO_2^{2-} or hydride anions increases, or that of carbon dioxide decreases, irrespective of the interpretation assumed. This causes an increase in the oxalate yield in the reaction product, in accordance with the influence of the concentration changes of basic and acidic species described in this paper.

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Zusammenfassung — Der einfluß von gasförmigen und festen Reaktanten auf die Ausbeute von oxalaten und Karbonaten bei der thermischen Zersetzung von Alkalimetallformiaten wurde untersucht. Es wurde ein Mechanismus für die Bildung dieser Produkte vorgeschlagen, der den Einfluß der während der thermischen Zersetzung von Alkalimetallformiaten entstehenden Basen und Säuren erklärt.

Резюме — Изучено влияние газообразных и твердых реагентов на выход оксалатов и карбонатов, получаемых при термическом разложении формиатов щелочных металлов. Предложен механизм образования этих продуктов реакции, который также объясняет влияние частиц основного и кислотного характера, образующихся в процессе термического разложения формиатов щелочных металлов.