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

\[ 2 \text{HCO}_2^- \rightarrow \text{H}_2 + \text{C}_2\text{O}_4^2^- \]  \hspace{1cm} (1)

\[ \text{H}_2 \text{O} \rightarrow \text{H}_2 + \text{CO}_3^2^- \]  \hspace{1cm} (2)

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\(_3\)ONa, 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
decompositions of the alkali metal formates were described earlier [12, 13]. The further transformations of the carbon species resulting from hydrogen evolution (CO\textsubscript{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\textsuperscript{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\textsubscript{1}, DTG\textsubscript{p}, DTA\textsubscript{p}, TG\textsubscript{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.