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THE THERMAL DECOMPOSITION OF HCOONa IN PRESENCE OF NaOH

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ABSTRACT

The run of the thermal decomposition of sodium formate in sodium formate - sodium hydroxide system has been examined thermoanalytically.

It has been found that sodium hydroxide being the reagent quantitatively reacting with sodium formate, keeps as the catalyst of the reaction of the thermal decomposition of sodium formate to sodium oxalate and that the selectivity of its catalytic action decreases if the concentration of oxygen in the atmosphere increases.

The solid products of the thermal decomposition of sodium formate there are sodium carbonate and sodium oxalate:

$$2\ HCOONa \rightarrow Na_2CO_3 + CO + H_2 \tag{1}$$

$$2\ HCOONa \rightarrow Na_2C_2O_4 + H_2 \tag{2}$$

As the last-mentioned product usually is the desirable one the selectivity related to sodium oxalate is the well-founded characterization of the process

$$S = \frac{n_{f2}}{n_{of}} \tag{3}$$

where n_{f2} is the number of sodium formate moles reacting according to the reaction (2), n_{of} is the initial (and under nonisothermal conditions also total) number of sodium formate moles. Let's characterize the composition of the mixture of sodium hydroxide and sodium formate by

$$a = \frac{n_{oh}}{n_{of}} \tag{4}$$

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where n_{oh} is the initial number of sodium hydroxide moles in the mixture.

It has been ascertained, that

- for $0 < a < 1$ also the solid mixtures of sodium carbonate and sodium oxalate,
- for $a = 1$ only sodium carbonate,
- for $a > 1$ the mixture of sodium carbonate and sodium hydroxide

are the products of the decomposition. The cases $a > 1$ are not interesting, so the mixtures of $0 < a < 1$ have been only examined.

It has been found, that the quantitative composition of thermal decomposition products of the mixtures examined depends on the mixture composition - a and on conditions of the decomposition process (the heating rate and the concentration of oxygen in the atmosphere).

In the case of oxygen-free atmosphere the dependence of the selectivity of the process on initial mixture composition ($0.02 < a < 1$) has the following form:

$$S = 1 - a \tag{5}$$

From (3), (4) and (5) one obtains

$$n_{f2} = n_{of} - n_{oh} \tag{6}$$

It means, that under the oxygen-free atmosphere sodium carbonate forms only in the reaction

$$\mathrm{HCOONa} + \mathrm{NaOH} \longrightarrow \mathrm{Na_2CO_3} + \mathrm{H_2} \tag{7}$$

and the remainder amount of sodium formate decomposes, at the same time, completely to sodium oxalate - the formation of sodium carbonate by the direct decomposition of sodium formate is suspended. The reaction scheme is then in this case following:

$$\begin{tikzcd} n_{of}\ \mathrm{HCOONa} + n_{oh}\ \mathrm{NaOH} \arrow[r] \arrow[dr] & n_{oh}\ (\mathrm{Na_2CO_3} + \mathrm{H_2}) \\ & \frac{1}{2}\ (n_{of} - n_{oh})\ (\mathrm{Na_2C_2O_4} + \mathrm{H_2}) \end{tikzcd} \tag{8}$$

It means, that under oxygen-free atmosphere sodium hydroxide being the reagent quantitatively reacting with sodium formate keeps as the catalyst of the reaction of the thermal decomposition of sodium formate to sodium oxalate (in the highest degree selective).

The dependence (5) maybe, in general, rewritten as:

$$S = S_2 (1 - a) \qquad (5.a)$$

where S_2 is the selectivity relating to the amount of sodium formate not reacting with sodium hydroxide ($n_{of} - n_{oh}$). Under oxygen-free atmosphere $S_2 = 1$ and it is independed of the heating rate (from 0.5 to 100 deg/min).

When the atmosphere contains oxygen the thermal decomposition process running in the sodium formate - sodium hydroxide system is (at nonisothermal conditions) two-stage one. The resolution of stages observed increases when the heating rate decreases. The dependence of the selectivity of the process on the initial mixture composition (similarly to the case of oxygen-free atmospheres) is linear but $S_2 < 1$ and this value decreases when the concentration of oxygen increases and/or the heating rate decreases. The reaction scheme is then:

$$\begin{array}{l} n_{of}\ HCOONa + n_{oh}\ NaOH \longrightarrow n_{oh} (Na_2CO_3 + H_2) \\ \qquad \longrightarrow \frac{1}{2} S_2 (n_{of} - n_{oh}) (Na_2C_2O_4 + H_2) \\ \qquad \longrightarrow \frac{1}{2} (1 - S_2) (n_{of} - n_{oh}) (Na_2CO_3 + CO + H_2) \end{array} \qquad (9)$$

The ascertaiment that under atmospheres containing oxygen S_2 1 means, that the catalytic selectivity of sodium hydroxide, which at this case keeps also as the catalyst of the thermal decomposition of sodium formate to sodium oxalate, is reduced by the oxygen action.