ORIGIN OF ORGANIC GASEOUS PRODUCTS FORMED IN THE THERMAL DECOMPOSITION OF FORMATES

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The gaseous products of the thermal decomposition of formates have been investigated and compared with the products of formaldehyde and synthesis gas transformation under analogous conditions in the presence of the solids formed in the thermal decomposition of particular formates. It was found that formaldehyde transformation leads to organic compounds identical to those obtained in the thermal decomposition of the respective formates, while synthesis gas does not react under such conditions. This fact substantiates the hypothesis that formaldehyde is a precursor of the organic compounds identified in the thermal decomposition of formates. The nature of the organic compounds obtained in the thermal decomposition of formates indicates that the formaldehyde formed in the initial stages is then transformed in the Cannizzaro or Tishchenko reactions.

Various gaseous compounds, both inorganic (H₂, CO, CO₂ and H₂O) and organic (HCHO [1-7], CH₄ [1-3, 8], HCO₂CH₃ [1, 2, 8], CH₃CH [1, 2], HCO₂H [9, 10], CH₃CHO [1], C₂H₄, C₂H₆ and CH₃OCH₃ [2]), have been identified among the products of thermal decomposition of different formates. The yield of inorganic products is usually greater than that of organic ones [1], and only inorganic compounds were found in some studies of the thermal decompositions of alkali metal formates [11] and transition metal formates [7, 12, 13].

The reported mechanisms of formation of organic products can be divided into two groups. In the first group of mechanisms it is accepted that synthesis gas (H₂ + CO) i; the precursor of the organic products [1, 4, 5, 11], whereas in the second group the precursor is formaldehyde [2, 3, 7]. It is assumed in both mechanisms that these precursors of the organic products are formed in the initial stages of thermal decomposition of the formates, and are then transformed in secondary reactions catalyzed by solid phases produced in the thermal decomposition of the formates.

In order to verify the above hypotheses, the gaseous products of thermal decomposition of formate have been studied in this work and compared with the
products of the formaldehyde and synthesis gas reactions proceeding in the presence of the solids resulting in the thermal decompositions of the formates. Formaldehyde reactions were carried out with fourteen metal oxides, two hydroxides and two carbonates. In the case of synthesis gas, negative results were obtained. Thus, only the experiments with two chosen metal oxides (SnO and ZnO) are presented here, for which the highest yields of organic compounds could be expected.

Experimental

Reactants

The following commercial formates (p.a. POCh, Poland) were used: HCO₂Na, HCO₂K, (HCO₂)₂Ca · H₂O, (HCO₂)₂Zn · 2H₂O, (HCO₂)₂Cd · 2H₂O, (HCO₂)₂Ni · 2H₂O and (HCO₂)₂Cu · 2H₂O. Other formates were prepared from the respective carbonates (p.a. POCh, Poland): HCO₂Li · xH₂O, HCO₂Rb · xH₂O, HCO₂Cs · xH₂O, (HCO₂)₂Sr · 2H₂O, (HCO₂)₂Ba, (HCO₂)₂Mn · 2H₂O, HCO₂Tl and (HCO₂)₂Pb, from the oxides (p.a. Merck): (HCO₂)₂Mg · 2H₂O and (HCO₂)₂Bi, or from the lanthanide oxides (p.a. BDH): (HCO₂)₃La and (HCO₂)₃Nd, and formic acid (p.a. POCh, Poland). Anhydrous bismuthyl formate HCO₂(BiO) was precipitated from an excess of ethanol treated with a hot solution of (HCO₂)₃Bi in formic acid [14]. (HCO₂)₂Fe · 2H₂O and (HCO₂)₂Sn were obtained through the exchange reactions of barium formate with the corresponding sulphates (p.a. POCh, Poland). (HCO₂)₂Hg₂ was obtained by treating freshly prepared HgO (from Hg(NO₃)₂ and NaOH; p.a. POCh, Poland) with a 20% solution of formic acid. Freely soluble salts were purified by recrystallization from water or alcohol solutions.

Gaseous formaldehyde was obtained from the depolymerization of paraformaldehyde (p.a. POCh, Poland). In place of the solid products obtained directly from the thermal decompositions of the respective formates, the following anhydrous compounds were used (p.a. POCh, Poland and SERVA): Li₂CO₃, Na₂CO₃, NaOH, Ba(OH)₂, Li₂O, Na₂O, CaO, SrO and BaO. The oxides ZnO, CdO, PbO, NiO and CuO were obtained from the thermal decompositions of the respective formates in an air atmosphere, and SnO from the decomposition of (HCO₂)₂Sn in a nitrogen atmosphere. CoO was obtained from the thermal decomposition of CoCO₃Co(OH)₂ (p.a. POCh, Poland) under nitrogen.

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