Thermochimica Acta, 89 (1985) 383–386
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

DECOMPOSITION OF COPPER(II), NICKEL(II) AND COBALT(II) FORMATES IN SELF-GENERATED ATMOSPHERES

A.A. VECHER, S.V. DALIDOVICH and E.A. GUSEV
Byelorussian State University, 220080 Minsk (U.S.S.R.)

(Received 31 January 1985)

At present, a lot of work has been dedicated to studies of the thermal decomposition of metal formates [1]. There are practically no papers dealing with investigations of the decomposition reactions of the above substances in self-generated atmospheres. Wendlandt studied the dehydration reaction of nickel formate in sealed ampoules and revealed the influence of the experimental conditions on the accuracy of determination of dehydration enthalpies [2]. A technique to study the pyrolysis of substances in self-generated atmospheres used in our work allowed us to obtain more exact values of the reactions enthalpies of the decomposition, of nickel, cobalt and copper formates.

EXPERIMENTAL

Nickel formate ($Ni(HCOO)_2 \cdot 2H_2O$) and cobalt formate ($Co(HCOO)_2 \cdot 2H_2O$) were prepared in a conventional way and were recrystallized from distilled water. Anhydrous salts were prepared by dehydration of the above crystallohydrates. Copper formate ($Cu(HCOO)_2$) was of reagent grade.

Thermal analysis was conducted within the range 150–700 K with a dynamic calorimeter of triple heat bridge type [3]. The heating rate was 2 K min^{-1} and the sample weight used was 28–32 mg. The substances were placed in stainless-steel ampoules having a volume of 0.9 cm^3. Such ampoules resisted pressure up to 10 MPa. Before sealing, the ampoules with samples were filled with Ar. After the decomposition of the samples the ampoules were cooled down to 100 K without being removed from the calorimeter and then they were reheated. Amounts of CO_2 and H_2O in the pyrolysis products were determined according to the peaks corresponding to CO_2 sublimation and H_2O melting and vaporization. Then the ampoules were opened and the composition of the gaseous products was analysed by means of a MAT-311 mass spectrometer and an LCM-69 chromatograph. Solid products of the reactions were analysed using a DRON-1,5 X-ray diffractometer.

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RESULTS AND DISCUSSION

The thermal curves of samples and their pyrolysis products are shown in Fig. 1. As one can see from Fig. 1 anhydrous nickel formate decomposes within the temperature range 535–600 K. The decomposition proceeds in several stages. The reaction begins from an exothermal effect, then there is a sharp endothermal effect and the process is completed with another exothermal effect. The shape of the thermal curve indicates that there are not only consecutive, but also parallel reactions. Evidently, the initial exothermal peak (at 541 K) is due to HCOH decomposition. HCOH is formed together with $NiCO_3$ in the first stages of the pyrolysis [4]. $NiCO_3$ then decomposes

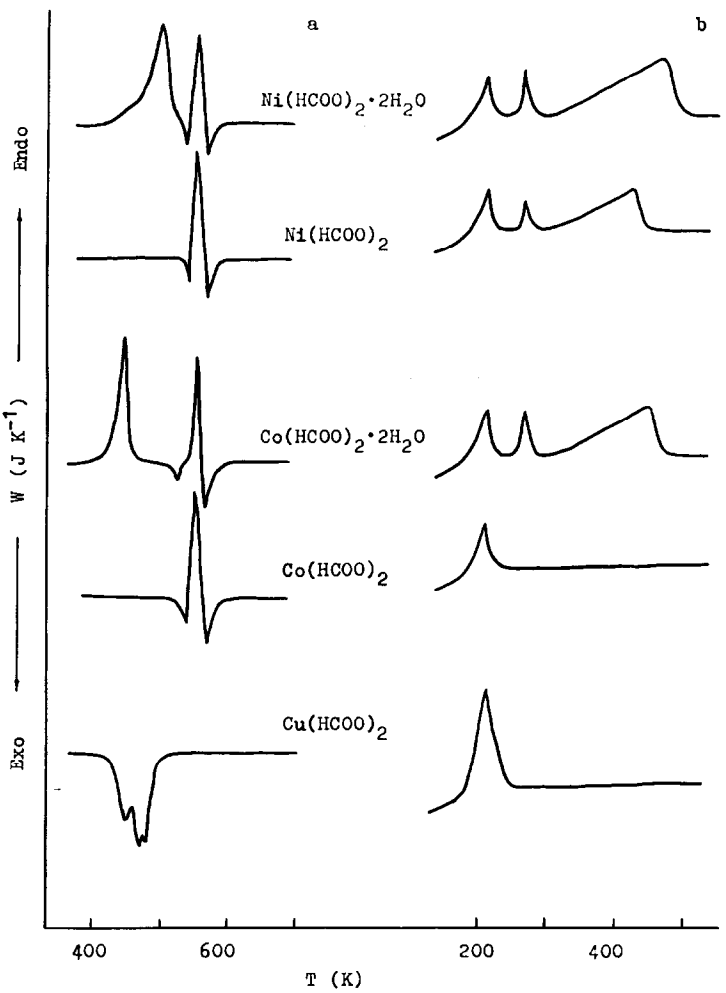

Fig. 1. Thermal curves of the formates' decomposition in sealed ampoules. (a) Initial substances, (b) products of their decomposition.

leading to a sharp endothermal peak (at 545 K) on the thermal curve. The decomposition ends with the reduction reaction of NiO by H_2 and CO. This reaction is accompanied by the evolution of heat (an exothermal peak at 562 K). The total enthalpy of the above chemical transformations is positive and at constant volume equals $+22 \pm 2$ kJ mol^{-1} (or $+34 \pm 2$ kJ mol^{-1} when recalculated at constant pressure). On the basis of the determination of the composition of nickel formate decomposition products one can propose the following equation for this reaction

$$2Ni(HCOO)_2 = 2Ni + 3CO_2 + 2H_2O + C$$

The estimation of the enthalpy of this reaction using data on enthalpies of formation of the above substances [5] gives $+42 \pm 16$ kJ mol^{-1}, a value which is in good agreement with that ($+34 \pm 2$ kJ mol^{-1}) obtained experimentally. The dehydration of nickel formate crystallohydrate takes place within the temperature range 440–520 K. At constant volume, the dehydration enthalpy amounted to $+109 \pm 5$ kJ mol^{-1}. Further heating of the sample gave the same thermal curve as in case of anhydrous $Ni(HCOO)_2$ (Fig. 1). Thus, one can suppose that the mechanisms of decomposition of crystallohydrate and anhydrous formate are identical, though there are some differences in their pyrolysis products.

$$2Ni(HCOO)_2 \cdot 2H_2O = 2Ni + 3CO_2 + 5H_2O + CO + H_2$$

Dehydration of $Co(HCOO)_2 \cdot 2H_2O$ takes place within the temperature range 430–470 K. At constant volume, the dehydration enthalpy reached $+104 \pm 5$ kJ mol^{-1}. Decomposition of $Co(HCOO)_2$ is observed within the range 510–570 K. A comparison of the thermal curves of nickel and cobalt formates shows that the mechanism of their decomposition reactions is complicated and identical. As it was shown by the analysis of the products, however, crystal water had no influence on $Co(HCOO)_2$ decomposition, unlike $Ni(HCOO)_2$, for the following reasons: (a) if we decompose an anhydrous sample, water is not found in the decomposition products (Fig. 1); (b) products of crystallohydrate pyrolysis contain the same quantity of water as that contained in the initial sample (in the form of crystal water). The enthalpy of decomposition of $Co(HCOO)_2$ was $+6.2 \pm 0.6$ kJ mol^{-1} at constant volume.

Unlike cobalt and nickel formates, copper formate decomposes within the range 430–500 K in several stages which are accompanied only by the evolution of heat. Total heat effect was -26 ± 2 kJ mol^{-1} at constant volume. On the basis of the results of the investigation of the decomposition of copper formate in sealed ampoules one can propose the following equation for its decomposition reaction

$$Cu(HCOO)_2 = Cu + 2CO_2 + H_2$$

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