Thermochimica Acta, 92 (1985) 235-239
Elsevier Science Publishers B.V., Amsterdam

THERMOANALYTICAL INVESTIGATION OF CITRIC ACID AND COMPLEXE SALDS OF THE TRANSITION METALS WITH CITRIC ACID

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ABSTRACT

Kinetic parameters of thermal decomposition of citric acid and complex salts of the metals with citric acid were investigated on the basis of the respective thermal curves. The values of the activation energy (E_a) of thermal decomposition, reaction ovder (n), frequency factor (A) and velocity constant (k) from thermo-analytical data were determined. In this paper we present too the thermofractochromatographic results.

INTRODUCTION

Metal citrates are often formed in natural systems, in verious conversions and in processes of food-stuffs manufacture [1]. Citric acid $C_6H_8O_7 \cdot H_2O$ is produced from glucose by yeasts [2]. In commercial manufacturing methods, an important stage is the separation of citric acid in the form of precipitated calcium citrate $Ca_3(C_6H_5O_7)_2$. It is hot precipitated as being easily separable from accompanying tartrates, oxalates and malates. Many processes, in the food industry, occuring at elevated temperatures are associated with the decomposition of citric acid or decomposition of formed metal citrates. It is, then, interesting to study the mechanism and stages of decomposition of such compounds.

MEASURING METHODS

Citric acid $C_6H_8O_7 \cdot H_2O$ (pure) by Zgierz - Poland and the prepared citrates of such metals as: Mg(II), Al(III), Ca(II),

Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) was taken for the investigations. Exsaminations of the pyrolysis were carried out by means of a Derivatograph 1000/1500 °C of the Paulik - Paulik - Erdey system produced by the Hungarian Optical Works MOM, Budapest. The thermograms were taken in the static atmosphere of air, using weighed portion of m_o = 500 mg. Other conditions were as follows: temperature range 20 - 1000 °C, heating rate 5°/min, DTA sensitivity 1/5, the recorder tape rate 1 mm/min [3, 4]. Thermofractochromatograms of the samples were made using a Thermofractochromatograph of our own Construction destribed in our paper [5]. The apparatus allows to carry out the investigations under nonisothermal conditions. A 0,5 mg sample placed in an open glass tube is heated in an oven at controlled temperature increase. The evaporating compounds in a neutral gas carrier are deposited directly into a thin - layer chromatography plate moving at a constant rate along the plane perpendicular to the capillary outlet of the tube. The development of chromatograms was carried out according to the procedure given in monographs [6 , 7].

RESULTS AND DISCUSSION

It can be seen from the thermoanalytical curves of the 10 metal citrates investigated under the static atmosphere of air that thermal decomposition occurs in four or five stages with the first stage being associated with the sample dehydration.

Eg. the thermal decomposition of $Mg_3(C_6H_5O_7)_2 \cdot 4H_2O$ takes place in the following 4 stages:

$$\text{I. } Mg_3(C_6H_5O_7)_2 \cdot 4H_2O \xrightarrow{373 - 423\ K} Mg_3(C_6H_5O_7)_2 \cdot 2H_2O + 2H_2O$$

$$\text{II. } Mg_3(C_6H_5O_7)_2 \cdot 2H_2O \xrightarrow{423 - 493\ K} Mg(C_6H_5O_7)_2 + 2H_2O$$

$$\text{III. } Mg_3(C_6H_5O_7)_2 \xrightarrow{495 - 613\ K} Mg_3(C_6H_3O_6)_2 + 2H_2O$$

$$\text{IV. } Mg_3(C_6H_3O_6)_2 + 9O_2 \xrightarrow{613 - 974\ K} 3MgO + 3H_2O + 12CO_2$$

with the formation of anhydrous salt, than magnesium aconitinate, magnesium carbonate and finally magnesium oxide and carbon dioxide.

Based on the obtained TG, DTG and T curves, the following kinetic parameters of the dehydration process were found: activation energy E_a, frequency factor A and reaction order n according to the procedure given in papers [8, 9]. Table 1 shows the obtained numerical values of kinetic parameters.

TABLE 1

Kinetic parameters E_a, n, A and k of the first partial proceses of the decomposition of metal complexes with citric acid during heat treatment in static air atmosphere.

Compound formula	Activation energy E_a kJ/mol	Order of reaction n	Value of A	Velocity constant k of reaction in temp 290K s^{-1}
1	2	3	4	5
$Zn_3(C_6H_5O_7)_2 \cdot H_2O$	44,1	0,6	$1,2\ 10^8$	$8,6\ 10^{-1}$
$Mn_3(C_6H_5O_7)_2 \cdot 9H_2O$	84,4	0,9	$1,1\ 10^9$	$4,3\ 10^{-2}$
$Cu_3(C_6H_5O_7)_2 \cdot 5H_2O$	69,9	0,6	$3,9\ 10^9$	$2,1\ 10^{-2}$
$Co_3(C_6H_5O_7)_2 \cdot 8H_2O$	54,9	1,3	$1,0\ 10^9$	$7,1\ 10^{-2}$
$Fe(C_6H_5O_7) \cdot 3H_2O$	49,0	1,4	$3,2\ 10^8$	$5,5\ 10^{-2}$
$Cr(C_6H_5O_7) \cdot 6H_2O$	59,1	1,0	$1,6\ 10^9$	$6,6\ 10^{-2}$
$Ni_3(C_6H_5O_7) \cdot 10H_2O$	65,0	0,8	$2,3\ 10^9$	$1,2\ 10^{-2}$
$Al(C_6H_5O_7) \cdot 4H_2O$	70,3	0,7	$3,1\ 10^{10}$	$9,8\ 10^{-2}$
$Mg_3(C_6H_5O_7)_2 \cdot 4H_2O$	72,4	0,8	$5,3\ 10^{10}$	$8,4\ 10^{-2}$
$Cn_3(C_6H_5O_7)_2 \cdot 4H_2O$	76,1	1,2	$4,2\ 10^{10}$	$7,8\ 10^{-2}$

The thermofractochromategrams of the investigated compounds obtained in the dynamic atmosphere of argon shows, that the thermal decomposition of metal citrates is a rather complicated process composed of several overlapping reactions.

CONCLUSIONS

1. Assuming values of T_n, i.e. the temperature at which a spot appears on the plate TLC as a volatility criterion one con state that the volatility of the citrates under investigation decreases in the ovder:

$$Zn > Al > Ni > Co > Fe > Mg > Cu > Mn > Ca > Cr$$

2. The values of the kinetic parameters indicate that when metal citrates are heated in the presence of oxygen at very low heating rates then ist oxidation occurs and a new substances are formed in the crucible.

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