Thermochimica Acta, 231 (1994) 151–159
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(93)01361-6

Chromium(III) compounds with valine and 2-amino benzoic (anthranilic) acid ligands. Thermal decomposition and kinetic study in air and argon atmosphere

M. Czerwiński [a], B. Kowalczyk [a,*] and P. Brągiel [b]

[a] *Institute of Chemistry, Pedagogical University, 42-200 Częstochowa (Poland)*
[b] *Institute of Physics, Pedagogical Univeristy, 42-200 Częstochowa (Poland)*

(Received 31 March 1993; accepted 14 May 1993)

Abstract

Thermal decomposition of chromium(III) compounds with valine and 2-amino benzoic (anthranilic) acid ligands has been studied up to 1000°C. Kinetic parameters of decomposition reactions have been calculated according to the Coats–Redfern method. Reaction paths are proposed and their agreement with the data from TG curves is checked.

INTRODUCTION

Complex compounds with amino acid ligands have been the focus of great interest within the past few years, mainly due to their cognitive importance as models of many metabolically active structures. Chromium(III) compounds are some of most widely investigated among them and it is well known that Cr(III) complex type compounds are involved in protein synthesis and lipid metabolism [1]. They are also of pharmacological importance, for instance in hypoglycaemia therapy [2].

Quite recently some new complex Cr(III) compounds with amino acids of the general formula R–CH(NH_2)–COOH (as follows from glycine) have been obtained [3]. Their magnetic properties, IR and EPR spectra are given elsewere [4].

Here, the results of a thermal decomposition and kinetic study of two compounds from this group, with valine (Val) and 2-amino benzoic (anthranilic) acid (Ant) ligands are reported.

---

[*] Corresponding author.

PREPARATION

The method of preparation for both compounds considered is the same and leads to tiny crystals [3]. 0.005 mol of $CrCl_3 \cdot 6H_2O$ is heated in 10 ml of water and 2 ml of ethanol. After the salt has dissolved to give a clear solution, 0.015 mol of amino acid is added. The mixture is further heated and mixed. When the solution is completely clear, part of the solvent is evaporated. At this point, in the case of anthranilic acid ligand, crystals of the complex are precipitated. To obtain the valine complex 0.002 mol of KOH is added to the warm solution. This is heated until fine crystals precipitate. Purification was carried out by recrystallization from water and water–ethanol solution. The compounds, $Cr(Ant)_3 \cdot H_2O$ and $Cr(Val)_3 \cdot 2H_2O \cdot KCl$, are green and pink crystallites, respectively. An elemental analysis gave results in excellent agreement with those calculated [3]. On the basis of magnetometric, spectroscopic (UVS, IR) and EPR measurements the structures shown in Fig. 1 have been proposed [3, 4].

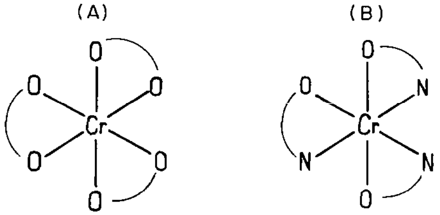

Fig. 1. Structures of the compounds under consideration: (A) $Cr(Ant)_3 \cdot H_2O$; (B) $Cr(Val)_3 \cdot 2H_2O \cdot KCl$.

EXPERIMENTAL

TG, DTG and DTA curves were recorded in air and in argon atmosphere using a Paulik–Paulik–Erdey derivatograph. The heating rate was 5 deg min^{-1} and all samples were heated to 1000°C.

CALCULATIONS

Thermogravimetric data give us the possibility of calculating the kinetic parameters for the decomposition reactions. The methods of calculation differ in the thermogravimetric curve approximation. For this work the method of Coats and Redfern has been chosen [5]. The thermogravimetric curve equation [6] is approximated in the form [7]

$$\log \frac{g(\alpha)}{T^2} = \log \frac{ZR}{qE}\left(1 - \frac{2RT}{E}\right) - \frac{E}{2.3RT} \tag{1}$$

where E is the activation energy, Z is a pre-exponential factor in the Arrhenius equation, $q = \mathrm{d}T/\mathrm{d}t$, α is the measure of conversion, $\alpha = (M_o - M)/(M_o - M_F)$, where M_o, M and M_F are, respectively, the initial, actual and final sample masses, and $g(\alpha) = \int_0^\alpha \mathrm{d}\alpha / f(\alpha)$ (conversion integral).

Function $f(\alpha)$ is taken in the form $f(\alpha) = (1 - \alpha)^n$, where n is the apparent reaction order. The further assumption, due to the $2RT/E$ value in the temperature range of interest is that eqn. (1) describes a straight line, $\log(g(\alpha)/T^2)$ versus $1/T^2$. The value of α is obtained from the TG curve, then $g(\alpha)$ is calculated, and the least squares fit to the straight line is obtained. The reaction order is treated as a free parameter during this procedure and the proper values are taken to be those which lead to the maximum value of Jaffe's correlation coefficient [8]. The FORTRAN code according Zsakó and Zsakó [7] was used to perform the necessary calculations.

RESULTS

TG, DTG and DTA curves for both complexes are given in Figs. 2(A) and 3(A) for air atmosphere and 2(B) and 3(B) for argon atmosphere, and the data characteristic of the thermal decomposition process are collected in Table 1. Kinetic parameters are given in Table 2.

Cr(Val)$_3$ · 2H$_2$O · KCl

The DTA curve in argon (Fig. 3(B)) indicates three decompositions which occur in the following range of temperatures: 70–150°C, 180–320°C and 320–400°C. The first and the third peaks are endothermic, while the second is without clearly defined character. The peak is very flat without a sharp maximum so it may be considered as the result of the superposition of two reactions having different energetic effects, following in the same temperature range. In air (Fig. 3(A)) the decomposition picture is simpler. There are only two peaks, between 60 and 140°C and between 200 and 480°C. The first is endothermic and the second exothermic in character. Calculated activation energies are smaller for the reactions in air atmosphere, but reaction orders are higher (see Table 2).

Cr(Ant)$_3$ · H$_2$O

Three peaks are seen on the DTA curve for $\mathrm{Cr(Ant)_3 \cdot H_2O}$, both in argon (Fig. 2(B)) and in air (Fig. 2(A)) atmosphere. The first are without unequivocal energetic character, the second ones are endothermic and the third peaks are exothermic. Peaks are recorded in a very similar range of

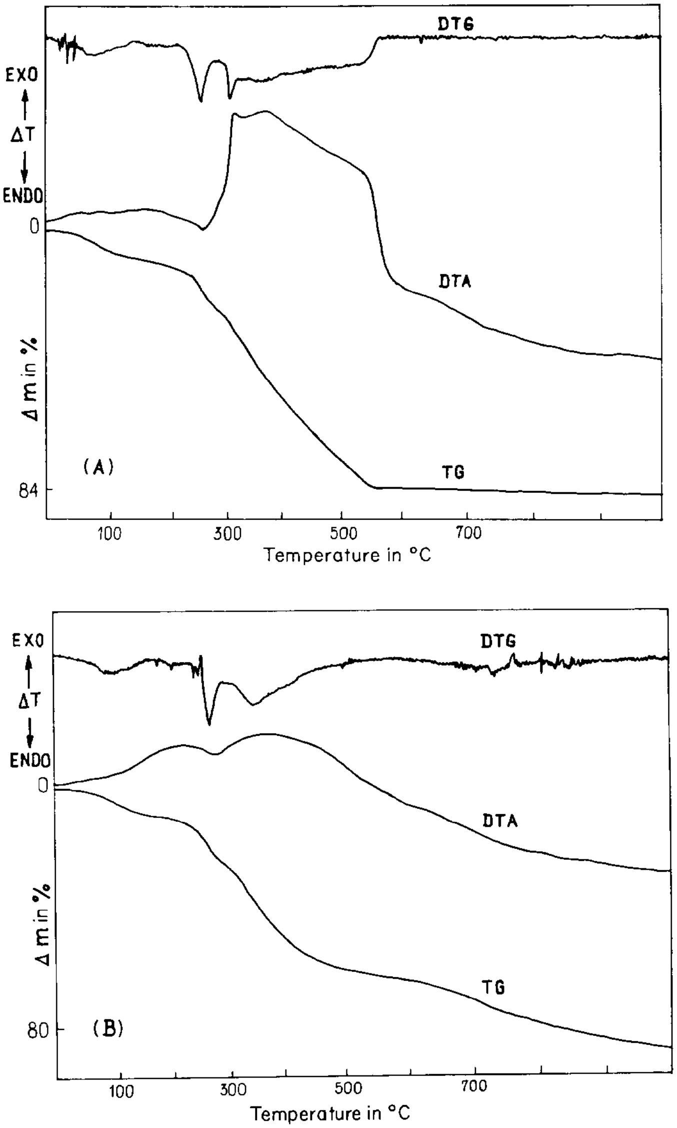

Fig. 2. DTG, DTA and TG curves for $Cr(Ant)_3 \cdot H_2O$ recorded in air (A) and argon (B) atmosphere. Heating rate, 5 deg min^{-1}.

temperatures: 60–200°C, 200–300°C, 300–580°C for argon and 60–180°C, 180–275°C and 275–560°C for air atmosphere. The final products of decomposition are solid Cr_2O_3 in air (subsequent to joining two molecules of the complex), and liquid CrO_3 in argon atmosphere. In the air atmosphere, good mass stabilization is achieved, in contrast to the situation

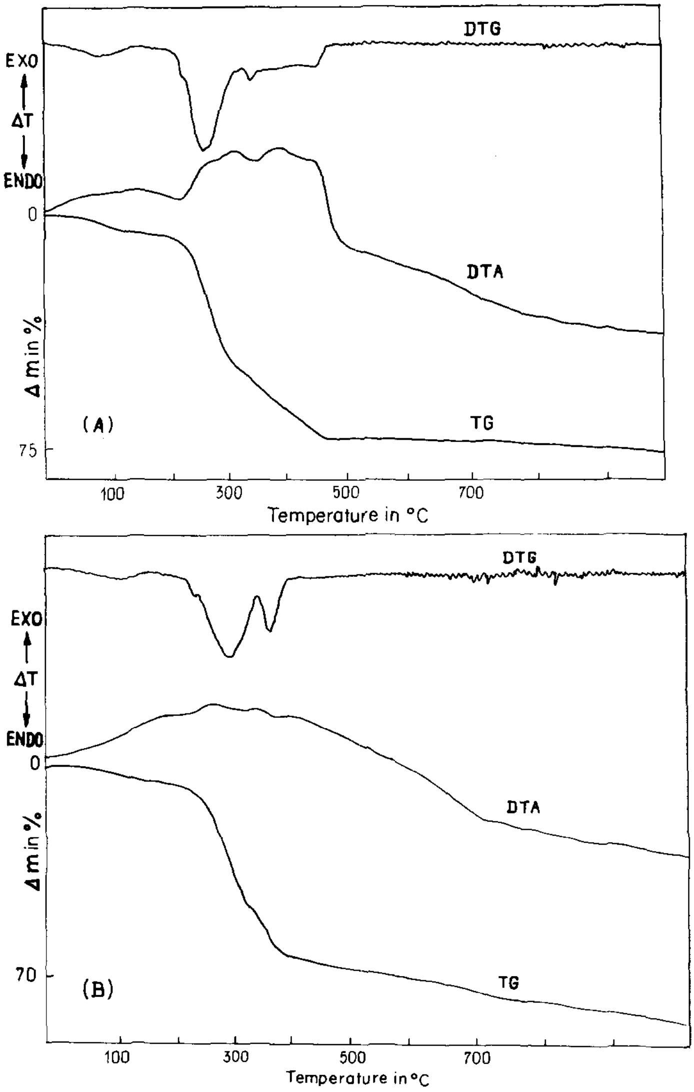

Fig. 3. DTG, DTA and TG curves for $Cr(Val)_3 \cdot H_2O \cdot KCl$ recorded in air (A) and argon (B) atmosphere. Heating rate, 4 deg min^{-1}.

observed in argon. This is probably the result of partial evaporation and decomposition of CrO_3.

Activation energies, as may be expected, are smaller in air, but in contrast to the case of the complex with valine ligands, apparent reaction orders have been found to be higher for the reaction in argon. There is an especially large difference for the third step of decomposition where *n* is over 5 in argon while it is under 2 in air.

TABLE 1

Thermal decomposition process characteristics[a]

Compound	Initial mass in μmol		Decomposition stage			Total Δm in %
			I	II	III	
$Cr(Val)_3 \cdot 2H_2O$		ΔT	60–140	200–480	–	
in air	97.37	T_{EX}	90ed	390ex		
		Δm	6.2	67.0		73.2
in argon	97.37	ΔT	70–150	180–320	320–400	66.2
		T_{EX}	90ed	ed/ex	380ed	
		Δm	6.2	43.0	17.0	
$Cr(Ant)_3 \cdot H_2O$		ΔT	60–180	180–275	275–560	
in air	103.95	T_{EX}	ed/ex	260ed	370ex	
		Δm	10.0	18.0	56.0	84.0
in argon	103.95	ΔT	60–200	200–300	300–580	
		T_{EX}	ed/ex	260ed	360ex	
		Δm	10.0	18.5	50.0	78.5

[a] ΔT is the range of temperatures for which Δm is indicated; T_{EX} indicates the temperature connected with DTA peak maximum: ex and ed indicate exothermic and endothermic decompositions, respectively; Δm is given for particular decompositions in percent. All the temperatures are given in °C and all the mass changes as % of the initial mass.

TABLE 2

Kinetic parameters[a] for thermal decomposition reactions

Compound	Decomposition[b]	E_a in kJ mol^{-1}	n	ln Z	Correlation factor, R
$Cr(Val)_3 \cdot 2H_2O \cdot KCl$					
in air	I	65.9	2.61	7.4	0.984
	II	113.4	5.42	8.9	0.989
in argon	I	45.6	1.56	3.9	0.993
	II	91.2	1.61	6.1	0.999
	III	200.4	1.43	14.0	0.992
$Cr(Ant)_3 \cdot H_2O$					
in air	I	74.3	4.10	8.7	0.980
	II	73.2	0.57	4.8	0.987
	III	51.3	1.87	1.2	0.993
in argon	I	68.9	3.79	7.7	0.998
	II	85.3	0.89	5.8	0.978
	III	158.5	5.32	11.0	0.999

[a] E_a is activation energy, n is reaction order and Z is the preexponential factor

[b] Peaks are numbered according rising temperature, see Figs. 2 and 3.

DECOMPOSITION REACTIONS

Thermogravimetric data are helpful when discussing the decomposition reaction patterns. Having recorded mass losses one can check if they are in accord with those calculated on the basis of an assumed reaction. To the best of our knowledge, there are no propositions concerning the possible decomposition paths for the compounds under consideration. In the following, we put forward some propositions for such reactions. They are reasonable in that they lead to mass losses which are in agreement with recorded ones. Full checking needs some additional investigations, including analysis of the products of particular steps of the reactions. At this stage, the reactions may be considered as follows.

$Cr(Ant)_3 \cdot H_2O$

In argon atmosphere, the decomposition products are gaseous ammonia and water, carbon monoxide, carbohydrates and liquid chromium oxide (Fig. 2(B)). The first step of the reaction is

$$Cr(C_6H_4NH_2COOH)_3 \cdot H_2O_{(s)} \rightarrow Cr(C_6H_4COO)_3 \cdot NH_3(s) + H_2O(g) + 2NH_3(g)$$

The calculated mass loss is 10.8%, while the recorded one is 10.0%. In the second step we have deeper rearrangement in the coordination sphere with mutual oxidation of the metal ion.

$$Cr(C_6H_4COO)_3(s) \rightarrow CrO_3(C_6H_4)_2 \cdot 3CO(s) + C_6H_4(g) + NH_3(g)$$

Calculated mass loss is 19.3% and the recorded one 18.5%. Finally, at the third step of decomposition we have

$$CrO_3(C_6H_4)_2 \cdot 3CO(s) \rightarrow CrO_3(l) + 2C_6H_4(g) + 3CO(g)$$

The total mass during the course of full decomposition as calculated from stoichometric relations is 79.2%; calculated from TG data it is 78.5%. We find this to be in good agreement.

In air atmosphere, the following reactions may be connected with the three observed peaks on the DTA curve (Fig. 2(A))

Peak 1

$$Cr(C_6H_4NH_2COOH)_3 \cdot H_2O(s) \rightarrow Cr(C_6H_4COO)_3 \cdot NH_3(s) + H_2O(g) + 2NH_3(g)$$

Peak 2

$$2Cr(C_6H_4COO)_3 \cdot NH_3(s) + O_2 \rightarrow 2CrO_3(C_6H_4)_2(C_7H_4)(s) + 4CO_2(g) + 2NH_3(g)$$

Peak 3

$2CrO_3(C_6H_4)_2(C_7H_4)(s) + 42.5O_2 \rightarrow Cr_2O_3(s) + 38CO_2(g) + 12H_2O(g)$

mass losses should be 10.8%, 18.6% and 54.8%; recorded decreases are 10.0%, 18.0% and 56.0% respectively.

Cr(Val)$_3$ ·2H$_2$O ·KCl

In argon atmosphere the first step is only the loss of water of crystallization.

$$Cr(C_4H_8NH_2COOH)_3 \cdot 2H_2O \cdot KCl(s)$$
$$\rightarrow Cr(C_4H_8NH_2COOH)_3 \cdot KCl(s) + 2H_2O(g)$$

This results in 7.0% mass decrease calculated from the reaction, compared with the recorded value of 6.2%.

In the second step the metal ion is oxidized with subsequent decomposition of the amino acid ligand

$$Cr(C_4H_8NH_2COOH)_3 \cdot KCl(s)$$
$$\rightarrow CrO_3(C_2H_4)_3 \cdot KCl(s) + 3NH_3(g) + 3CO(g) + 3C_2H_4(g)$$

The sample mass decrease due to the reaction should be 42.6%; the experimental value is 43.0%.

At the last step, at temperature over 320°C, destruction of the coordination sphere takes place

$$CrO_3(C_2H_4)_3 \cdot KCl(s) \rightarrow CrO_3(l) + KCl(s) + 3C_2H_2(g)$$

with a predicted mass loss equal to 16.3%, while the recorded value is 17.0%.

In air atmosphere, there are only two steps, but these are more complicated. Decomposition, as in argon, starts with loss of water, but in the same range of temperatures, oxidation of chromium and the joining of two molecules take place.

$$2Cr(C_4H_8NH_2COOH)_3 \cdot 2H_2O \cdot KCl + 3O_2$$
$$\rightarrow 4H_2O(g) + 2CrO_3(C_4H_8NH_2COOH)_3 \cdot KCl(s)$$

$$2CrO_3(C_4H_8NH_2COOH)_3 \cdot KCl(s) + 45O_2$$
$$\rightarrow Cr_2O_3 \cdot 2KCl(s) + 30CO_2(g) + 33H_2O(g) + 6NO_2(g)$$

The calculated mass losses are 6.6% and 66.6% and the measured ones 6.2% and 67.0%, respectively, for the first and the second reaction.

ACKNOWLEDGEMENTS

We thank Dr K. Giełzak-Koćwin for providing us with samples and Professor W. Wojciechowski for helpful comments and remarks.

REFERENCES

1 E.J. Underwood, Trace Elements in Human and Animal Nutrition, 4th edn., Academic Press, New York, 1977.
2 J.A. Cooper, L.F. Blackwell and P.D. Buckley, Inorg. Chim. Acta, 92 (1984) 23.
3 K. Giełzak, Ph.D. Thesis, Katowice, 1991.
4 K. Giełzak-Koćwin and W. Wojciechowski, J. Alloys Compds., in press.
5 A.W. Coats and J.P. Redfern, Nature, 210 (1968) 68.
6 C.D. Doyle, J. Appl. Polym. Sci., 15 (1961) 285.
7 J. Zsakó and J. Zsakó, Jr., J. Therm. Anal., 19 (1980) 333.
8 H.H. Jaffe, Chem. Rev., 53 (1953) 191.