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Thermal decomposition and kinetic study of chromium(III) complexes with serine and glutamic acid ligands

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Abstract

Results from TG, DTA and DTG measurements have been obtained for $Cr(Ser)_3 \cdot H_2O \cdot 3KCl$ and $Cr_2(OH)_2(Glu)_3 \cdot 2H_2O \cdot KCl$, up to 1000 °C, in both air and argon atmospheres. Decomposition reactions are proposed and the resulting mass losses compared with those obtained from experimental data. The kinetic parameters of the decomposition reactions are calculated within the framework of the Coats–Redfern method.

Keywords: Atmosphere; Chromium compound; Coats–Redfern; Decomposition; DTA; DTG; Kinetics; TG

1. Introduction

Complexes with amino acid ligands, which are models of biologically active structures, have been widely investigated [1]. Chromium(III) compounds, which are one of the most interesting, were found to be involved in lipid metabolism and protein synthesis [2]. Chromium(III) compounds of this type are also helpful in hypoglyceamia therapy [3].

Recently, some new Cr(III) compounds with ligands of general formulae $R–CH(NH_2)–COOH$ have been obtained [4]. Magnetic properties, and infrared

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and electron spin resonance spectra, together with suggestions concerning their structure, are given elsewhere [4,5].

Here we report the results of the thermal decomposition study, supplemented with calculation of the kinetic parameters for the observed decomposition reactions for Cr(III) compounds with serine (Ser) and glutamic acid (Glu) ligands.

2. Preparation

The compounds $Cr(Ser)_3 \cdot H_2O \cdot 3KCl$ and $Cr_2(OH)_2(Glu)_3 \cdot 2H_2O \cdot KCl$ were obtained in almost the same way [4]. $CrCl_3 \cdot 6H_2O$ (0.005 mol) was heated in 10 ml of water and 2 ml of ethanol. When the salt was dissolved, 0.015 mol of aminoacid was added, and the mixture was further heated until the solution became clear. The solution was then reduced in volume by evaporation, and 0.002 mol of KOH was added to the warm solution. The solution was heated until precipitation of fine crystals in the case of the glutamic acid complex, and to complete evaporation of the solvent in the case of the serine complex. The complexes were recrystallized from water and water–ethanol solution. The compounds $Cr(Ser)_3 \cdot H_2O \cdot 3KCl$ and $Cr_2(OH)_2(Glu)_3 \cdot 2H_2O \cdot KCl$ form raspberry red and violet crystals, respectively. Elemental analysis results are in very good agreement with the proposed formula for the compounds [4].

3. 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 K min^{-1}, and all samples were heated up to 1000°C.

Thermogravimetric data are helpful in discussing the decomposition reactions. Having recorded the mass losses, one can check to see if they are in accordance with those calculated on the basis of the assumed reaction. There are no previously proposed decomposition paths for the compounds under consideration. The mass losses calculated for the decomposition reactions proposed here are in agreement with recorded values. Some additional investigations, particularly the analyses of the products in each step of the reactions, are useful.

4. Calculations

The thermogravimetric data enable us to calculate the kinetic parameters of the decomposition reactions. The methods of calculation differ in the thermogravimetric curve approximation. For the purpose of this work, the method of Coats and Redfern was chosen [6]. The thermogravimetric curve equation [7] is approximated in the form [8]

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

where E is the activation energy, Z the pre-exponential factor in the Arrhenius equation, $q = \mathrm{d}T/\mathrm{d}t$, α the measure of conversion, $\alpha = (M_0 - M)/(M_0 - M_F)$, M_0, M, M_F being the initial, actual and final sample masses, and

$g(\alpha) = \int_0^a \frac{\mathrm{d}\alpha}{f(\alpha)}$, the conversion integral.

The 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 $2RT/E$ values in the relevant temperature range, is that Eq. (1) describes a straight line, i.e. $\log(g(\alpha)/T^2)$ 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. The best value is obtained when Jaffe's correlation coefficient reaches a maximum value [9]. A Fortran code was used to perform the necessary calculations [8].

5. Results and discussion

The TG, DTG and DTA curves for the investigated complexes are given in Figs. 1 and 2 for air and argon atmospheres, respectively, and the data for the thermal decomposition processes are listed in Table 1. The kinetic parameters are given in Table 2.

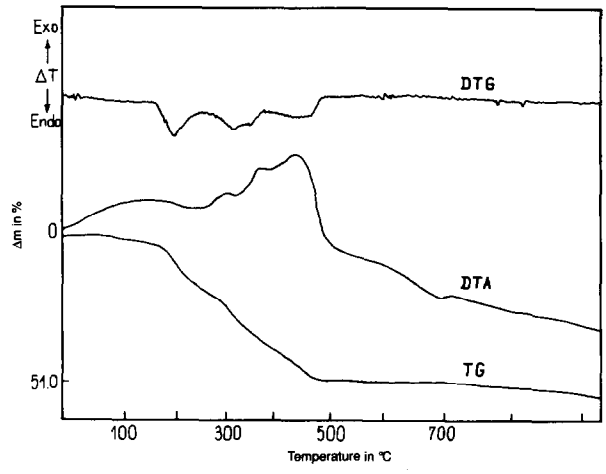
5.1. $Cr(Ser)_3 \cdot H_2O \cdot 3KCl$

The DTA curve in argon atmosphere (Fig. 2a) indicates three decompositions in temperature ranges 80–240, 240–380 and 380–670°C. The first and third have no clear energetic character; the second peak is exothermic. From the TG curve, the decomposition products were determined as gaseous ammonia and water, carbon monoxide, hydrocarbons and solid chromium oxide. The total mass loss during the course of the full decomposition was calculated to be 46.8% and the recorded value was 48.1%. The calculated mass losses in the particular steps were 20.2%, 17.4% and 9.2%; the recorded values were 19.0%, 18.5% and 10.6%, respectively. The following reactions are associated with these decompositions

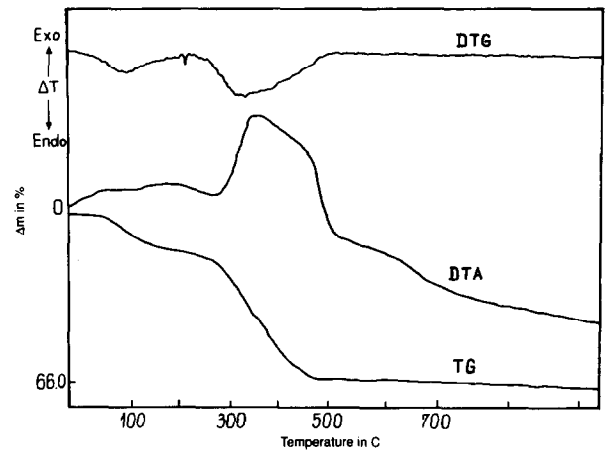
$$Cr(HO \cdot CH_2CH \cdot NH_2 \cdot COOH)_3 \cdot H_2O \cdot 3KCl(s) \rightarrow$$
$$4H_2O(g) + 3NH_3(g) + Cr(C_2H_2COO)_3 \cdot 3KCl(s)$$

$$Cr(C_2H_2COO)_3 \cdot 3KCl(s) \rightarrow 3C_2H_2(g) + CO(g) + CrO_3 \cdot C_2O_2 \cdot 3KCl(s)$$

$$CrO_3 \cdot C_2O_2 \cdot 3KCl(s) \rightarrow CrO_3 \cdot 3KCl(s) + 2CO(g)$$



(a)



(b)

Fig. 1. TG, DTG and DTA curves recorded in air atmosphere. a. $Cr(Ser)_3 \cdot H_2O \cdot 3KCl$. b. $Cr_2(OH)_2(Glu)_3 \cdot 2H_2O \cdot KCl$.

In an air atmosphere (Fig. 1a), the DTA curve shows two peaks in the ranges 110–140 and 245–540°C. The first has no clearly defined character, the second is exothermic. From the TG curve, the mass losses should be 15.0% and 35.8%; recorded mass losses were 16.0% and 35.0%, respectively. The products were water, ammonia, carbon dioxide and $Cr_2O_3 \cdot KCl$ (solid). There were no hydrocarbon products. The calculated total mass loss is 50.8%, while the recorded value was 60.0%. The decomposition reactions are

$$2Cr(HO \cdot CH_2CH \cdot NH_2 \cdot COOH)_3 \cdot H_2O \cdot 3KCl(s) + 1.5O_2 \rightarrow$$

$$2CrO_2(C_2H_2COO)_3 \cdot 3KCl(s) + 7H_2O(g) + 6NH_3(g)$$

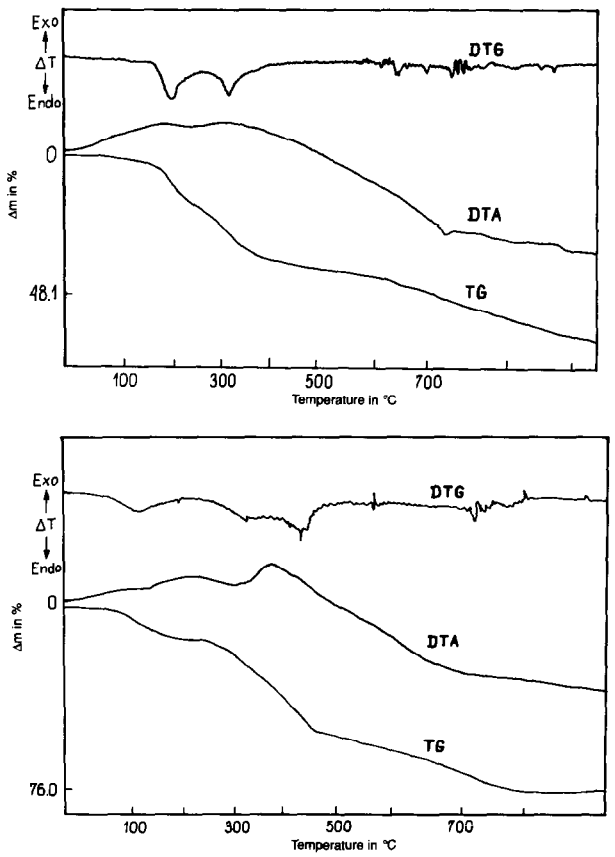


Fig. 2. TG, DTG and DTA curves recorded in argon atmosphere. a. $Cr(Ser)_3 \cdot H_2O \cdot 3KCl$. b. $Cr_2(OH)_2(Glu)_3 \cdot 2H_2O \cdot KCl$.

$$2CrO_2(C_2H_2COO)_3 \cdot 3KCl(s) + 14.5O_2 \rightarrow$$
$$18CO_2(g) + 6H_2O(g) + Cr_2O_3 \cdot 6KCl(s)$$

5.2. $Cr_2(OH)_2(Glu)_3 \cdot 2H_2O \cdot KCl$

Four peaks are observed on the DTA curve (Fig. 2b) recorded in argon atmosphere. The first and last are without clearly defined character; the other peaks are exothermic. Peaks are recorded in the temperature ranges 60–115, 115–320, 320–470 and 470–740°C. From the TG curve, the mass losses, as calculated for particular steps, should be 5.2%, 12.2%, 26.6% and 32.5%; the recorded mass losses are 5.0%, 12.0%, 28.0% and 31.0%, respectively. The following decomposition reactions may occur, the calculated total mass loss is 76.5%; the recorded one was 76.0%

Table 1
Thermal decomposition process characteristics

	Initial mass/μmol		Decomposition stage				Total Δm%
			I	II	III	IV	
$Cr(Ser)_3 \cdot H_2O \cdot 3KCl$							
In air	82.17	ΔT	110–245	245–540			
		T_{EX}	ed/ex	440_{ex}			
		Δm%	16.0	35.0			51.0
In argon	82.17	ΔT	80–240	240–380	380–670		
		T_{EX}	ed/ex	300_{ex}	ed/ex		
		Δm%	19.0	18.5	10.6		48.1
$Cr_2(OH)_2(Glu)_3 \cdot 2H_2O \cdot KCl$							
In air	72.51	ΔT	60–170	170–500			
		T_{EX}	ed/ex	370_{ex}			
		Δm%	13.0	53.0			66.0
In argon	72.51	ΔT	60–115	115–320	320–470	470–740	
		T_{EX}	ed/ex	220_{ex}	380_{ex}	ed/ex	
		Δm%	5.0	12.0	28.0	31.0	76.0

Key: ΔT, range of temperatures for which Δm is indicated; T_{EX} indicates the temperature of the DTA peak maximum; ex and ed indices are used for exothermic and endothermic decompositions, respectively. All the temperatures are given in °C; all the mass changes in % of the initial mass.

Table 2
Kinetic parameters for thermal decomposition reactions

	Decomposition	E_a/ kJ mol^{-1}	n	ln Z	Correlation factor, R
$Cr(Ser)_3 \cdot H_2O \cdot 3KCl$					
In air	I	94.2	1.96	8.2	0.997
	II	59.2	2.20	2.3	0.990
In argon	I	38.0	0.39	1.4	0.989
	II	80.8	1.56	4.7	0.998
	III	50.9	1.68	0.5	0.973
$Cr_2(OH)_2(Glu)_3 \cdot 2H_2O \cdot KCl$					
In air	I	55.2	2.48	5.5	0.997
	II	62.4	2.15	2.5	0.999
In argon	I	73.9	1.23	8.3	0.998
	II	16.4	0.89	−1.2	0.937
	III	89.6	1.43	4.3	0.997
	IV	58.5	0.59	0.2	0.986

Key: E_a, activation energy; n, reaction order; Z, pre-exponential factor.
[a] Peaks are numbered according to rising temperature, see Figs. 1 and 2.

$$Cr_2(OH)_2(C_5H_9O_4N)_3 \cdot 2H_2O \cdot KCl(s) \rightarrow$$
$$2H_2O(g) + Cr_2(OH)_2(C_4H_9O_3N \cdot CO)_3 \cdot KCl(s)$$
$$Cr_2(OH)_2(C_4H_9O_3N \cdot CO)_3 \cdot KCl(s) \rightarrow$$
$$3CO(g) + Cr_2(OH)_2(C_4H_9O_3N)_3 \cdot KCl(s)$$
$$Cr_2(OH)_2(C_4H_9O_3N)_3 \cdot KCl(s) \rightarrow$$
$$3CO_2(g) + 3NH_3(g) + Cr_2(OH)_2(C_3H_6O)_3 \cdot KCl(s)$$
$$Cr_2(OH)_2(C_3H_6O)_3 \cdot KCl(s) \rightarrow (C_3H_6O_{0.33})_3(g) + H_2O(g) + Cr_2O_3 \cdot KCl(s)$$

In air (Fig. 1b), the decomposition is simpler. There are only two peaks: in the ranges 60–170 and 170–500°C. The first is without clearly defined character; the second one is exothermic. The final product is solid $Cr_2O_3 \cdot KCl$, in both argon and air atmosphere. Sample mass decreases, due to the above reactions, should be 12.6% and 54.6%; experimental values were 13.0% and 53.0%, respectively.

$$Cr_2(OH)_2(C_5H_9O_4N)_3 \cdot 2H_2O \cdot KCl(s) \rightarrow$$
$$3NH_3(g) + 2H_2O(g) + Cr_2(OH)_2(C_5H_6O_4)_3 \cdot KCl(s)$$
$$Cr_2(OH)_2(C_5H_6O_4)_3 \cdot KCl(s) + 14.5O_2 \rightarrow$$
$$15CO_2(g) + 10H_2O(g) + Cr_2O_3 \cdot KCl(s)$$

The sample mass decrease due to the above reactions should be 67.2%; the experimental value was 66.0%.

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