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THERMAL DECOMPOSITION OF THE $[Co(NH_3)_6]Cl_3$, $Co[(NH_3)_4Cl_2]Cl$, $K_3[Fe(C_2O_4)_3]3H_2O$ AND $Fe(CH_3COO)_3$ IN ARGON AND AIR ATMOSPHERE

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Kinetic parameters (apparent activation energy, reaction order, pre-exponential factor (Z) in the Arrhenius equation) for thermal decomposition of the $[Co(NH_3)_6]Cl_3$, $Co[(NH_3)_4Cl_2]Cl$, $K_3[Fe(C_2O_4)_3]3H_2O$ and $Fe(CH_3COO)_3$ are reported. They have been calculated on the DTA and TG data according to Coats-Redfern's model. Both, decomposition data obtained in argon and in air atmosphere have been considered and the results are compared.

The studies of thermal decomposition of transition metal complex compounds have attracted great interest for many years. Efforts were also made to estimate the kinetical parameters from thermal data using different computational methods. In this paper results of DTA, TG and DTG studies for ferric acetate, potassium-ferric oxalate, hexaamino cobalt(III) trichloride and tetraaminodichlorocobalt(III) chloride are reported together with activation energy, reaction order and Z factor calculations. Although three of this compounds have been previously studied [12-16], calculations of kinetical parameters have been done only for ferric acetate [13]. There are not comparative studies in air and in inert atmosphere for all of them as well.

Experimental

Compounds for TG measurements were prepared and purified according to the methods described by Supniewski [1] and Brauer [2]. Their purity was

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Table 1 Thermal decomposition process characteristics

Compounds	Initial mass [μMol]		Decomposition stage I	II	III	IV	Total, ΔM [%]	Final, temp.
$K_3[Fe(C_2O_4)_3].3H_2O$	203.68	ΔT	60-125	260-290	290-315	315-550	43.50	550
		T_{EX}	110_{ed}	280_{ex}	300_{ex}	375_{ed}		
in air		ΔM	13.0	17.02	7.99	5.5		
	203.68	ΔT	50-140	250-375	375-410	410-550	50.32	550
		T_{EX}	105_{ed}	250_{ex}	400_{ed}	420_{ed}		
in argon		ΔM	10.0	18.33	14.0	7.99		
$Fe(CH_3COO)_3$	429.31	ΔT	175-265	265-340	–	–	63.0	340
		T_{EX}	130_{ex}	310_{ex}				
in air		ΔM	31.0	32.0				
	429.31	ΔT	120-250	250-350	–	–	63.0	350
		T_{EX}	190_{ex}	260_{ex}				
in argon		ΔM	31.0	32.0				

Table 1. continued

Compounds	Initial mass [μMol]		Decomposition stage I	II	III	IV	Total, ΔM [%]	Final temp.
$Co[(NH_3)_4Cl_2]Cl$	428.42	ΔT	50-200	200-280	800-950	–	54.2	950
		T_{EX}	100_{ed}	250_{ex}	920_{ed}			
in air		ΔM	20.0	25.0	9.2			
	428.42	ΔT	80-185	185-380	830-900	–	54.1	900
		T_{EX}	100_{ed}	200_{ed}	880_{ed}			
in argon		ΔM	20.0	24.9	9.2			
$[Co(NH_3)_6]Cl_3$	376.86	ΔT	225-300	300-410	410-850	–	75.3	850
		T_{EX}	270_{ed}	358_{ed}	650_{ex}			
in air		ΔM	32.7	21.8	20.8			
	373.86	ΔT	215-295	295-390	700-950	–	79.9	950
		T_{EX}	280_{ed}	350_{ed}	850_{ed}			
in argon		ΔM	34.0	18.0	27.9			

ΔT - range of temperatures for which ΔM is indicated, in ^{o}C; T_{EX} indicates the temperature connected with DTA peak maximum; final temperature-temperature at which mass stabilisation is achived; *ex* and *ed* indicies are used for exothermic and endothermic decompositions, respectively; ΔM for particular decompositions in percent. All the temperatures are given in ^{o}C, all the mass changes in % of the initial mass checked by elemental analysis and its UV spectra was compared with the literature data.

TG, DTG and DTA curves were recorded, in air and in argon, using a derivatograph. All samples were heated up to 1000° with the 5 deg/min rate.

Calculations

Applying TG curves data it is possible to calculate the kinetical parameters of the decomposition reaction. There are several methods for this purpose which differ in the way of the thermogravimetric curve approximation (e.g. Redfern [5], Freeman - Carroll [3], Fuosse [4] methods). Coats - Redfern's method [5] - has been used which is usually in good agreement with the results of Freeman-Carroll and Fuosse methods [9,10].

Calculations are based on the approximation of the thermogravimetric curve equation [8] to the form [7]:

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

where

E is an activation energy,

Z is a pre-exponential factor in the Arrhenius equation,

$q = \frac{dT}{dt}$ and α is the measure of the conversion ($\alpha = \frac{M_O - M}{M_O - M_F}$, M_O, M, M_F are initial, actual and final sample massies),

and $g(\alpha)$ is so called conversion integral, $g(\alpha) = \int\limits_0^\alpha \frac{d\alpha}{f(\alpha)}$.

Function $f(\alpha)$ is taken as $f(\alpha) = (1\text{-}\alpha)^n$ where n is apparent reaction order (see [7] for details).

As $2RT/E$ for the interesting range of temperatures and typical values of E is small comparing to *1*, we are able to assume Eq. (1) to describe a straight line: $\log\frac{g(\alpha)}{T^2}$ *vs.* $\frac{1}{T^2}$

Value of α is determined from TG curve and then, after finding $g(\alpha)$, the least square fit to the straight line is obtained. Reaction order, (n), is changed during calculations - proper value is indicated by the maximum of the Jaffe's correlation coefficient [11]. Code according Zsakó and Zsakó [7] has been used in calculations reported in this paper.

Results

TG and DTA curves for all the considered compounds, recorded in argon and in air, are presented on the Figs 1-2. Kinetical parameters for the reactions are collected in Table 2. In the following a brief description of the recorded curves is given.

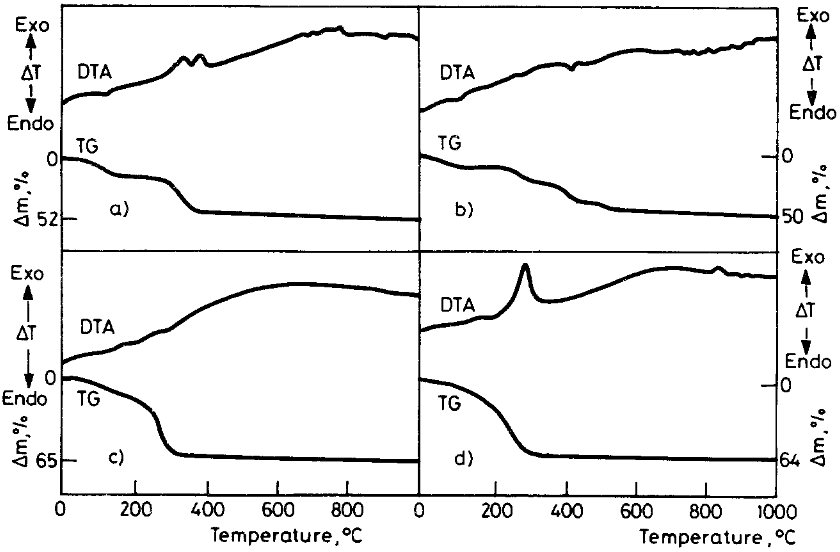

Fig. 1 TG and DTA curves of potassium Fe(III) oxalate in air (1a) and in argone (1b); Fe(III) acetate in air (1c) and in argone (1d)

$K_3[Fe(C_2O_4)_3]mH_2O$

On the DTA curve (in argon) peaks for four thermal decompositions are seen (up to 550°) - Fig. 1b. Three of them are endothermic and have been recorded in the following temperature range: 50-140°, 375-410° and 410-450°. The fourth decomposition, in the range of 250-375°, is exothermic in character. DTA curve recorded in air (Fig. 1a) is quite different: we have two endothermic peaks, 60-125° and 335-550°, and two exothermic ones at 260-295° and 295-335°.

Table 2. Parameters for thermal decomposition reactions

Compound	Decomposition*	E_a, kJ/mol	n	ln Z	Correlation factor, R
$K_3[Fe(C_2O_4)_3].3H_2O$	I	36.7	1.23	2.4	0.996
	II	740.2	1.89	71.2	0.993
in argon	III	263.9	0.80	18.0	0.993
	IV	1372.8	1.90	101.7	0.995
	I	91.5	1.47	10.2	0.997
in air	II	319.3	1.86	27.8	0.990
	III	801.8	1.87	71.6	0.995
	IV	353.0	1.84	28.2	0.994
$Fe(CH_3COO)_3$	I	111.6	1.69	10.6	0.993
in argon	II	178.8	1.77	14.2	0.994
in air	I	99.1	1.52	8.1	0.992
	II	176.6	1.51	15.6	0.967
$[Co(NH_3)_6]Cl_3$	I	151.9	1.80	12.3	0.994
	II	188.7	1.77	14.0	0.994
in argon	III	162.3	2.75	5.0	0.982
	I	144.8	1.73	11.8	0.994
	II	268.7	2.92	21.2	0.997
in air	III	117.2	2.59	4.1	0.997
$Co[(NH_3)_4Cl_2]Cl$	I	74.9	1.69	3.9	0.932
	II	78.1	3.12	5.5	0.981
in argon	III	898.1	2.86	3.9	0.992
	I	153.5	6.72	19.7	0.983
	II	259.1	1.51	26.6	0.999
in air	III	1361.1	2.06	56.9	0.989

* peaks are numbered according rising temperature, see Figs 1-2

E_A - activation energy; n - reaction order; Z - preexponential factor

$Fe(CH_3COO)_3$

$Fe(CH_3COO)_3$ is thermally decomposed in lower temperatures then $K_3[Fe(C_2O_4)_3]3H_2O$. The character of the DTA curve is the same both in air (Fig. 1c) and in argon (Fig. 1d); two exothermal peaks have been observed. The slighty difference is that in argon decomposition starts in lower temperature, peaks are in the following ranges: 120-250°, 250-350° in argon and 175-265° and 265-340° in air.

$[Co(NH_3)_6]Cl_3$

Hexaaminocobalt(III) trichloride thermal dissociation occurs in three stages: in argon (Fig. 2b) all the conversions, 215-295°, 295-390° and 700-950°, are endothermic, whereas in air (Fig. 2a) one, 410-850°, is exothermic and the two others, 225-300° and 300-400°, are endothermic.

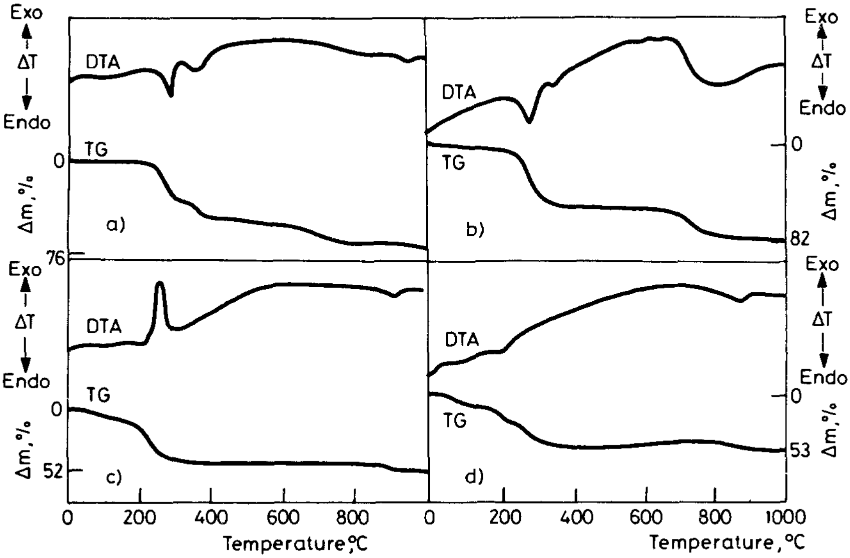

Fig. 2 TG and DTA curves of hexaaminocobalt(III) chloride in air (2a) and in argone (2b); tetraamino-dichlorocobalt(III) chloride in air (2c) and in argone (2d)

$Co[(NH_3)_4Cl_2]Cl$

Three decompositions have been recorded for tetraaminodichlorocobalt(III)chloride, both in argon and in air. In argon (Fig. 2d) decomposition of this compound is started with wide endothermic peak at 80-185°. The next conversion, also endothermic, occurs between 185 and 380°. Decomposition is ended with high temperature endothermic conversion at 830-900°. In air (Fig. 2c) decomposition begins in lower temperatures (50-200°) and ends at higher ones (900-950°). Both this stages are endothermic. The third one, in the range 200-380°, is strongly exothermic.

Full characteristics of the all decomposition steps recorded - mass losses, extreme temperature of the decomposition and temperature in which mass stabilization is achived is given is Table 1.

Decomposition reactions

Termogravimetric measurements give the possibility to check the proposed path of the thermal decomposition reaction. Decomposition path has been previously proposed for three of the considered compounds [13-16]; in this cases we have verified that our data are concerted with earlier propositions. Decomposition of the potassium-ferric oxalate has not been described yet, only results for $K_3[Cr(C_2O_4)_3]3H_2O$ have been given [12] but, according to our data, decomposition path for both these salts must be slightly different.

Let us start the more detailed discussion with the amino compounds.

Thermal decomposition of the trichlorohexaaminocobalt has been previously described by Watt [15] and Wendtland [16]. Decomposition products are solid $CoCl_2$ and gaseous N_2, NH_3 and NH_4Cl. The reactions may be given as follows:

In air the first step:

$$6[Co(NH_3)_6]Cl_3 \rightarrow 6\text{trans-}Co[(NH_3)_4Cl_2]Cl_{(s)} + 12NH_{3(g)}$$

$$6Co[(NH_3)_4Cl_2]Cl_{(s)} \rightarrow 3CoCl_2 + 3(NH_4)_2CoCl_{4(s)} + N_{2(g)} + 16NH_{3(g)}$$

$$6Co[(NH_3)_6]Cl_3 \rightarrow 3CoCl_{2(s)} + 3(NH_4)_2CoCl_{4(s)} + N_{2(g)} + 28NH_{3(g)},$$

The second step:

$$3(NH_4)_2CoCl_{4(s)} \rightarrow 3CoCl_{2(s)} + 6NH_4Cl_{(g)}.$$

Our data are in good accordance with this reaction. For the first step mass loss is 31.5% as calculated from stoichiometric relations while it is calculated from TG data is 32.7%. For the second step sample mass decrease should be, due to reaction, 20.0%; calculated from our data is 21.8%. The third peak we have found for $[Co(NH_3)_6]Cl_3$, exothermic one at 650°, has not been previously described. It is probably due to the thermal decomposition of $CoCl_2$ with cobalt oxidation to $CoOCo_2O_3$:

$$6CoCl_2 \xrightarrow{+O_2} 2Co_3O_{4(s)} + 6Cl_{2(g)}$$

Mass loss from this reaction is expected to be 18.5%; recorded is 20.8%. Total mass loss during the course of the full decomposition process, is 75.3%; according to our proposal the mass at the end of the process should be 70%. This difference may be due to instoichiometry of the Co_3O_4 - the amount of the CoO is greater than it can be expected from stoichiometrical relations.

In the argon the two first steps of the decomposition are the same as in the air. Measured losses are 34.0% and 18.0% instead of the expected 31.5% and 20.0% respectively. Third peak, recorded in this case at higher temperatures, may be treated as a consequence of

$$6CoCl_2 \rightarrow 6Co_{(s)} + 6Cl_{2(g)}$$

decomposition. Mass loss should be 26.5% in fact 27.9% decrease has been recorded. The problem is that the measured total mass loss is 79.9% whereas the 22% of the sample mass is the mass of metal. Sublimation of cobalt is rather inprobable so we think that this is the effect of an unaccuracies accumulation starting from analytical checking of the sample purity.

$Co[(NH_3)_4Cl_2]Cl$ TG curves in nitrogen have been recorded by Ocone *et al.* [14]; the same compound has been studied by Watt [15]. Conclusion from this studies is that decomposition proceeds to NH_3 and solid $CoCl_2$. $CoCl_2$ mass stabilization is achieved at 380° [15]. This picture is in agreement with our results. If we wanted to describe a more detailed scheme it could be given as follows:

$$6Co[(NH_3)_4Cl_2]Cl \rightarrow 3CoCl_{2(s)} + 3(NH_4)_2CoCl_{4(s)} + N_{2(g)} + 16NH_{3(g)}$$

$$3(NH_4)_2CoCl_4 \rightarrow 3CoCl_{2(s)} + 6NH_4Cl_{(g)}$$

$$6CoCl_2 \rightarrow 2(Co_2CoCl_2)_{(s)} + 2Cl_{2(g)}$$

Mass losses calculated from this reactions are 21.5%, 22.9% and 10.1% when those from TG curves are 20.0%, 24.9% and 9.2% respectively. The second step is ended in 380^0 which is strictly the same temperature that has been found by Watt [15]. The third step reaction has been chosen to fit the recorded mass loss; as this peak has been recorded for the first time there are no any data for comparison. Total mass loss should be 54.5%, while the recorded is 54.1%.

In the air decomposition takes place in a different way. The most visible appearance of this difference is the exothermic character of the second peak. The first step is the same as in argon - during the course of the second one, however, the solid products are partially oxidized:

$$3(NH_4)_2CoCl_4 \xrightarrow{+O_2} 6NH_4Cl_{(g)} + CoO\ 2CoCl_{2(s)} + Cl_{2(g)}.$$

Calculated mass loss for this reaction is 28% whereas recorded one is 25%. Remaining solid products are decomposed and oxidized at the higher temperatures (third step):

$$3CoCl_2 + CoO\ 2CoCl_2 \xrightarrow{+O_2} Co_3O_4\ 3CoCl_{2(s)} + 2Cl_{2(g)}$$

Expected mass loss is 6.7%, recorded one is 9.2%. During the full process mass is expected to be 56.2% decreased; recorded loss is 54.1%.

Fe(III) acetate decomposition has been studied by Jewur and Kuriacose [13]. They have found that decomposition carries out Fe_2O_3, CO_2 and CH_3COCH_3. This picture matches our data too. Mass loss during the reaction

$$2Fe(CH_3COO)_3 \rightarrow Fe_2O_{3(s)} + 3CH_3COCH_{3(g)} + 3CO_{2(g)}$$

is 65.7% when one obtained from TG curve is 63.0%. Similar agreement is between activation energy values given is Jewur's an Kuriacose's paper - 110.4kJ/mol - and our ones see Table 2.

There is however an important difference between previous and our results: Jewur and Kuriacose have found both peaks to be endothermic whereas in our DTA measurements exothermic effects are recorded. Especially for the case of the air atmosphere the second peak is strongly exothermic (Fig. 1c) due to the atmosphere. On the other hand however TG curves are almost the same and the mass changes for both cases support the same scheme of the decomposition.

Thermal decomposition reactions of the $K_3[Fe(C_2O_4)_3]$ have not been described yet; TG studies have been done by House and Blumenthal for $K_3[Cr(C_2O_4)_3]$, [12]. Some analogies may be expected, but only for the first two steps of decomposition. The final solid product is expected to be K_3CrO_3 [12] so for the iron homologue at least a last step should be different. The full decomposition path may be as follows:

In argone

$$2K_3[Fe(C_2O_4)_3]3H_2O \rightarrow 2\,K_3[Fe(C_2O_4)_3]_{(g)} + 6H_2O_{(g)}$$

$$2K_3[Fe(C_2O_4)_3] \rightarrow 2\,K_3[Fe(C_2O_4)(CO_3)(CO)]_{(s)} + 4CO_{2(g)}$$

$$2K_3[Fe(C_2O_4)(CO_3)(CO)] \rightarrow 2K_3[Fe(CO_3)_2]_{(s)} + 4CO_{(g)}$$

$$2K_3[Fe(CO_3)_2] \rightarrow 2FeO_{(s)} + 3K_2CO_{3(s)} + CO_{(g)}.$$

Mass losses calculated according to the above reactions are 11.0%, 17.9%, 11.4% and 5.7% respectively. Values from the experimental data are, in the same order, 10.0%, 18.3%, 14.0%, and 8.0%.

In the air the two first steps are the same; the next two ones are of the following forms:

$$2K_3[Fe(C_2O_4)(CO_3)(CO)] \xrightarrow{+O_2} 2K_3[Fe(CO_3)_2(O)]_{(s)} + 4CO_{2(g)}$$

$$2K_3[Fe(CO_3)_2(O)] \rightarrow Fe_2O_{3(s)} + 3K_2CO_{3(s)} + CO_{(g)}.$$

Mass changes, calculated and found, are 8.1% and 8.0% for the first of the above reactions, 5.7% and 5.5% for the second one respectively. Total change is calculated to be 42.7% whereas measured value is 43.5%.

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Zusammenfassung — Es werden die kinetischen Parameter (scheinbare Aktivierungsenergie, Reaktionsordnung, präexponentieller Faktor (Z) der Arrhenius-Gleichung) der thermischen Zersetzung von $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_4Cl_2]Cl$, $K_3[Fe(C_2O_4)_3]3H_2O$ und $Fe(CH_3COO)_3$ beschrieben, die entsprechend dem Coats-Redfern-Modell auf der Basis der DTA- und TG-Daten errechnet wurden. Die Zersetzung wurde sowohl in Argon als auch in Luft durchgeführt und die erhaltenen Daten miteinander verglichen.