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KINETIC ANALYSIS OF THERMOGRAVIMETRIC DATA XXXII. DSC study of some $[Co(Diox{\cdot}H)_2(amine)_2]X$ and $H[Co(Diox{\cdot}H)_2(N_3)_2]$ type complexes with alicyclic α-dioximes*

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Abstract

14 mixed Co(III) dioximine chelates of the types $[Co(Diox{\cdot}H)_2(amine)_2]X$ (X = Br, I, NO_3, ClO_4) and $H[Co(Diox{\cdot}H)_2(N_3)_2]$, respectively ($Diox{\cdot}H_2$-1,2-cyclohexane dione dioxime (nyoxime), 1,2-cycloheptane dione dioxime (heptoxime) 1,2-cyclooctane dione dioxime (octoxime) were obtained and their thermal decompositions were studied in an argon atmosphere. After the dehydration of the crystallohydrates, both types of complexes exhibit 3 decomposition stages. For the $[Co(Diox{\cdot}H)_2(amine)_2]X$ type complexes (X = Br, I) the first endothermal stage is the substitution of an amine molecule for the external sphere anion and this process is followed by two exothermal decomposition stages. With $H[Co(Diox{\cdot}H)_2(N_3)_2]$ type complexes the first and third processes are relatively slow, but the second process is very fast, corresponding to a vertical portion of the TG curves. From the TG curves kinetic parameters were derived for 11 processes and the validity of a non-linear compensation law was observed.

Keywords: dioximine complexes of Co, DSC, kinetic compensation effect, kinetic parameters of thermal decomposition

Introduction

The first chelates with the lower homologues of these ligands were obtained by Wallach [1]. The Ni(II), Pd(II) and Fe(II) derivatives have been used for the analytical determination of these metals [2, 3]. In our previous papers [4–10] a series of mixed cobalt(III) chelates: $[Co(Diox{\cdot}H)_2(amine)_2]X$, $[Co(Diox{\cdot}H)_2X(amine)]^0$ and $[Co(Diox{\cdot}H)_2]X_2]^{n-}$ (X – halide, pseudohalide: NCS^-, $NCSe^-$; NO_2^-, N_3^-, SO_3^{2-}, $S_2O_3^{2-}$; $Diox{\cdot}H_2$ – alicyclic α-dioximes with 5–8 C atoms in the hydroaromatic ring) were obtained by means of the classical

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air oxidation of the components in dilute alcoholic solutions, and by substitution reactions, respectively.

In this work 14 mixed chelates: $[Co(Niox{\cdot}H)_2(amine)_2]X$ and $H[Co(Diox{\cdot}H)_2(N_3)_2]$ type complexes were obtained and characterized (Table 1).

The middle IR spectra of these compounds show the presence of short, strong intramolecular O···H···O hydrogen bonds, which stabilize the $Co(Diox{\cdot}H)_2$ moiety in the equatorial plane of the octahedral structure (ν_{O-H} 2300–2400 cm^{-1} (m–s), $\delta_{O-H\cdots O}$ 1700–1800 cm^{-1} (w). The $\nu_{C=N}$ and ν_{N-O} bands 1550–1560 cm^{-1} (s) and 1240 (v.s.) 1090–1100 cm^{-1} (v.s.) are shifted and split as compared to the free oximes ($\nu_{C=N}$ 1620–1630 cm^{-1}, ν_{N-O} 980–1060 cm^{-1}), showing the strong covalent character of the Co–N bonds [11]. The $\nu_{C-N_{oxime}}$ and $\nu_{C-N_{amine}}$ frequencies appear at 510–520 cm^{-1} and 480–490 cm^{-1}. The bands at 320 cm^{-1} and 280 cm^{-1} in the far IR region can be assigned to the $\delta_{N_{ox}-Co-N_{ox}}$ and $\delta_{N_{am}-Co-N_{am}}$ vibrations [12].

It is worth mentioning that with increasing size of the hydroaromatic ring, the intensities of the ν_{C-H} (2940–2960, 2870–80 cm^{-1}(s, v.s.)) and of the δ_{CH_2} (1440–1450, 1370–1380 cm^{-1} (m–s)) bands also increase.

The thermal decomposition of $[Co(Diox{\cdot}H)_2(amine)_2]X$ type complexes with $Diox{\cdot}H_2$–dimethylglyoxime or diphenylglyoxime [13–15], investigated by means of thermogravimetry, showed that if the external sphere anion is a halogen or pseudohalogen, such as NCS^- or $NCSe^-$, the first stage of the thermal decomposition is a substitution reaction.

$$[Co(Diox{\cdot}H)_2(amine)_2]X \rightarrow [Co(Diox{\cdot}H)_2(amine)X] + amine \qquad (1)$$

i.e. an amine ligand is substituted for the external sphere anion, the liberated amine is volatilized and a nonelectrolytic compound is formed as a relatively stable intermediate.

The same substitution reaction (1) has been observed if an alicyclic α-dioxime played the role of the co-ordinated Diox·H ligand. For this purpose 1,2-cyclopentane.., -cyclohexane.., -cycloheptane.. and -cyclooctane dione dioxime derivatives have been used [16–21].

In all cases apparent kinetic parameters have been derived from the TG curves recorded in an air atmosphere under dynamic temperature conditions, by using a constant heating rate. For deriving these parameters, different calculation techniques have been used [22–26]. In some cases TG curves have been recorded under different working conditions and the influence of the heating rate and sample mass upon the kinetic parameters derived have been investigated [14, 20, 21].

Generally, between the apparent activation energy E and the pre-exponential factor A, derived from TG curves, a correlation can be observed, known as kinetic compensation effect. Frequently, the above kinetic parameters obey a linear compensation law:

Table 1 $[Co(Diox{\cdot}H)_2(amine)_2]X$ and $H[Co(Diox{\cdot}H)_2(N_3)_2]$ type complexes

No.	Formula	Mol. mass calcd.	Appearance (microscop.)	Analysis/%		
					calcd.	found
I.	$[Co(Niox{\cdot}H)_2(o\text{-ethylaniline})_2]I$	710.5	brown hexagonal plates	Co N	8.3 11.8	8.1 11.4
II.	$[Co(Niox{\cdot}H)_2(o\text{-ethylaniline})_2]Br{\cdot}H_2O$	681.5	brown prisms	Co	8.6	8.3
III.	$[Co(Niox{\cdot}H)_2(m\text{-amino-phenol})_2]Br{\cdot}4H_2O$	729.1	brown hexagonal prisms	Co	8.1	8.0
IV.	$[Co(Niox{\cdot}H)_2(p\text{-Cl-aniline})_2]I{\cdot}H_2O$	741.3	sparkling, brown hexagonal plates	Co N	7.9 11.3	7.6 11.5
V.	$[Co(Niox{\cdot}H)_2(p\text{-Br-aniline})_2]Br{\cdot}0.5H_2O$	774.2	brown stars	Co	7.7	7.6
VI.	$[Co(Niox{\cdot}H)_2(p\text{-toluidine})_2]Br$	635.5	brown quadrat. prisms	Co N	9.2 13.2	9.1 13.0
VII.	$H[Co(Niox{\cdot}H)_2(N_3)_2]$	426.3	sparkling brown dendrites	Co N	13.8 32.9	13.5 32.1
VIII.	$H[Co(Heptox{\cdot}H)_2(N_3)_2]{\cdot}3H_2O$	508.3	sparkling brown plates	Co N	11.6 27.7	11.3 28.2
IX.	$H[Co(Octox{\cdot}H)_2(N_3)_2]{\cdot}2H_2O$	518.4	thin brown dendrites	Co N	11.4 27.0	11.2 26.6
X.	$[Co(Niox{\cdot}H)_2(p\text{-Cl-aniline})_2]NO_3$	658.2	brown prisms	Co	8.9	9.0
XI.	$[Co(Niox{\cdot}H)_2(p\text{-Br-aniline})_2]ClO_4$	784.8	brown quadrat. prisms	Co N	7.5 10.7	7.4 11.2
XII.	$[Co(Niox{\cdot}H)_2(p\text{-Cl-aniline})_2]ClO_4$	695.6	thin needles	Co	8.5	8.2
XIII.	$[Co(Niox{\cdot}H)_2(p\text{-toluidine})_2]ClO_4$	655.0	long, brown needles	Co	9.0	8.7
XIV.	$[Co(Niox{\cdot}H)_2(p\text{-toluidine})_2]NO_3$	617.5	brown prisms	Co	9.5	9.5

$Niox{\cdot}H_2$ – 1,2-cyclohexane dione dioxime; $Heptox{\cdot}H_2$ – 1,2-cycloheptane dione dioxime; $Octox{\cdot}H_2$ – 1,2-cyclooctane dione dioxime

$$\log A = aE + b \tag{2}$$

The validity of relation (2) for the substitution reactions (1) has been observed [27].

The validity of the linear relation (2) implies the existence of an isokinetic temperature T_i. If, for n-set of reactions there is a given temperature T_i at which the rate constants of all the reactions have the same value k_i, from the Arrhenius' equation the following relation can be derived [28]:

$$\log A = \frac{E}{RT_i \ln 10} + \log k_i \tag{3}$$

Since, under the conditions of TG analysis, the rate constant becomes practically different from zero at the decomposition temperature, at the beginning of the thermal decomposition there will be a relatively narrow temperature interval in which the rate constants will be very near to each other, i.e. the temperature T_i in Eq. (3) will be a certain decomposition temperature [28].

It is very difficult to define exactly the decomposition temperature. This is why it was proposed to take $T_{0.1}$ for this isokinetic temperature [29]. $T_{0.1}$ means the temperature at which the conversion of the substance, undergoing thermal decomposition, is equal to 0.1. Thus, instead of $a=(RT_i \ln 10)^{-1}$, the parameter

$$a' = \frac{1}{RT_{0.1} \ln 10} \tag{4}$$

can be defined, where $T_{0.1}$ stands for the arithmetic mean of the $T_{0.1}$ values of all the reactions of the set considered [29].

In the case of reaction (1), the parameter a of Eq. (2) is very near indeed to a' defined by Eq. (4) [20, 21].

Although a and a' are almost equal if the $T_{0.1}$ values are close to each other, irrespective of the nature of the thermal decomposition reaction [30], the validity of Eq. (2) is limited. The correlation between E, A and $T_{0.1}$ obeys a non-linear law, which may be given as [31]

$$\log A' = \frac{E'\tau_{0.1}}{R \ln 10} + \log E' + \log \tau_{0.1}^2 + \log q - 4.85 \tag{5}$$

In the above relationship $\tau_{0.1}=10^3 T_{0.1}^{-1}$, R is expressed in J K^{-1}, E' in kJ, the heating rate q in K s^{-1}.

As shown, A', the 'theoretical' pre-exponential factor is practically equal to the pre-exponential factor A derived directly from the TG curve [31].

In the present work some new representatives of $[Co(Diox{\cdot}H)_2(amine)_2]X$ type complexes as well as three azido-complexes were also obtained and their thermal decompositions investigated.

Experimental

The $[Co(Niox{\cdot}H)_2(amine)_2]X$ type complexes were obtained by bubbling air through a dilute alcoholic solution (1:3) of the mixture: $Co(acetate)_2{\cdot}4H_2O$, nyoxime and amine (molar ratio: 1:2:3), followed by precipitation with an excess of NaX (*X*=Br, I, NO_3, ClO_4) [9–10].

The free $H[Co(Diox{\cdot}H)_2(N_3)_2]$ acids were obtained from the solution of the sodium salts with an excess of 20% H_2SO_4, washed with diethyl ether and dried in air.

Analysis: The Co content was determined complexometrically after destroying the samples (80–100 mg) with boiling H_2SO_4 + some crystals of KNO_3. The *N* content was determined with the usual microanalytical method.

The thermal measurements were carried out with a 951-TG and DSC calorimeter (DuPont Instruments) in an argon atmosphere. Sample mass 5–6 mg, heating rate 10 K min^{-1}.

The far IR spectra were measured with a BIO-Rad-Ninn spectrophotometer in polyethylene pellets, while the middle FTIR spectra with a Perkin-Elmer 2000 apparatus in KBr pellets.

Results and discussion

The Co dioximine complexes No. I–IX. from Table 1 were investigated. If *X*=NO_3, ClO_4, the binary salts (X–XIV) decompose suddenly, generally with explosion, without well defined decomposition stages.

A DSC study was also performed, by recording both the TG and heat flow curves in an argon atmosphere, by using a constant heating rate of 10 K min^{-1}.

The decomposition of the crystallohydrates begins at lower temperatures, leading to the loss of water. The characteristics of these dehydration processes are given in Table 2.

Table 2 Characteristics of the dehydration reactions

Compound	$T_{0.1}$/ K	Δm/ moles of H_2O	DSC peak temp./ K	Q/ kJ mol^{-1}
II.	353	0.95	–	–
III.	332.5	3.87	363.8	108.8
IV.	358	0.91	368	–
V.	393	0.47	399	9.0
VIII.	370	2.96	–	–
IX.	383	1.73	–	–

The mass loss Δm during this stage is expressed in moles of H_2O per mole of complex. Obviously, the mass losses are consistent with the above given molecular formulae, by taking into account that under dynamic temperature conditions the complete elimination of the volatile product is not possible up to the apparent stop of the mass loss. All these reactions are endothermal and the position of the endothermal peaks are consistent with the TG curves, although these temperatures are lower than T_m corresponding to the maximum decomposition rate. This shift is not surprising since the working conditions (shape of sample holder, mass of the sample) are not identical. The interpretation of the heat values Q, obtained by integrating the heat flow curves, is not easy, since we have only two values. Taking into account that compound III. contains 4 moles of H_2O, and V. only 0.5 moles, the great difference between the Q values seems to be reasonable.

The decomposition of the anhydrous $[Co(Niox{\cdot}H)_2(amine)_2]X$ type complexes begins with an endothermal process, which presumably consists of the substitution reaction (1).

As seen from Table 3, the mass losses Δm are consistent with this hypothesis, except for compound IV. for which the mass loss is higher, i.e. reaction (1) is overlapped by a further decomposition. This might be due to the high decomposition temperature of compound No. IV., favouring also other pyrolysis processes. $T_{0.1}$ is higher only for compound VI. For this complex the end of reaction (1) is marked on the TG curve only by a small inflexion and the substitution is followed by a rapid exothermal decomposition process.

Table 3 Characteristics of the substitution reaction

Compound	$T_{0.1}$/ K	Δm/ moles of amine	Endothermal peak temp./ K	Q/ kJ mol^{-1} of complex	Q'/ kJ mol^{-1} of liberated amine
I.	437	0.94	427.4	53.2	56.6
II.	444	0.89	437.2	62.2	69.9
III.	467	0.69	456.5	32.1	46.5
IV.	468	1.29	467.2	61.8	47.9
V.	464	0.83	467.7	51.1	61.6
VI.	525	0.86	518.0	–	–

From Table 3 it is obvious that $T_{0.1}$ generally increases from compound I. to VI. This increasing decomposition temperature might mean an increasing bond strength between the donor amine ligand and the central Co atom. All amine ligands investigated are aniline derivatives. In VI. the amine ligand contains an electron repulsing substituent favouring the formation of the N–Co bond. In the complexes III., IV. and V., the amine ligand has electron withdrawing substi-

tuents, therefore the N–Co bond becomes weaker and $T_{0.1}$ lower. Although in I. and II., the substituent of the amine ligand has electron repulsing effect, its orthoposition entails the weakening of the N–Co bond, due to steric hindrances, which overcompensate the electronic effect and makes compounds I. and II. the least stable among the complexes studied.

Obviously, the endothermal peak temperatures are mostly lower than $T_{0.1}$. This means that in the samples for heat flow measurements the pyrolysis processes occur at slightly lower temperatures than under the conditions of TG analysis.

Q values are of the same order of magnitude. Since up to the stop of mass loss the conversion of reaction (1) is not the same, we calculated also a Q' value, meaning the heat per one mole of liberated amine. This procedure makes the heat values a little more uniform, viz., the relative standard deviation of Q values from their arithmetic mean is 0.21, and that of Q' is only 0.15.

Nevertheless, one cannot even try to find a correlation between Q' and the nature of the leaving amine and of the entering X. It is worth mentioning that in the calculation of Q' the conversion obtained in the TG measurement was used, but in the sample for heat flow measurements the conversion might be different.

In the case of compounds I.–VI. reaction (1) is followed by two exothermal processes. Their characteristics are presented in Table 4.

Table 4 Exothermal processes of the decomposition of compounds I–VI

Compound	First stage			Second stage		
	Peak temp./ K	Q/ kJ mol^{-1}	Δm/ %	Peak temp./ K	Q/ kJ mol^{-1}	Δm/ %
I.	513.8	95	29	528	–	4
II.	516	45	35	545.1	223	2
III.	478	102	12	532	–	7
IV.	483	86	15	534.8	102	6
V.	516.8	30	20	544.9	132	5
VI.	527.3	80	36	541	–	3

As seen, the first stage is more important, leading to the volatilization of a significant part of the sample. No correlation can be found between the nature of the amine ligand and either the DSC peak temperatures or the Q values.

The thermal decomposition of compounds VII.–IX. is completely different. It consists of three stages, the second one being very fast, almost explosion like, is marked on the TG curves by a vertical portion and a very large mass loss. In this stage a part of the sample might be even thrown out of the sample holder. The first and the last stage are relatively slow, allowing the $T_{0.1}$ values to be determined.

The characteristics of these stages are given in Table 5. Obviously, the temperature of the second stage, as well as the $T_{0.1}$ value of the third stage increase in the order

$$\text{Niox·H} < \text{Heptox·H} < \text{Octox·H},$$

i.e. with the size of the cycle in the dioxime ligand. Δm decreases in the second stage and increases in the third stage in the same order. The explanation for these features is not clear.

Table 5 Decomposition stages of compounds VII–IX

Compound	Stage 1		Stage 2		Stage 3	
	$T_{0.1}$/ K	Δm/ %	$T_{0.1}$/ K	Δm/ %	$T_{0.1}$/ K	Δm/ %
VII.	453	10	488	48	613	5
VIII.	433	18	538	36	673	15
IX.	455	18	573	25	763	30

Derivation of kinetic parameters

For several decomposition stages the TG curves were sufficiently well defined to allow kinetic parameters to be derived. For this purpose the nomogram method [25, 29, 32] was used. For the corresponding stages, by using the TG curves, the temperatures $T_{0.1}$, $T_{0.5}$ and $T_{0.9}$, corresponding to conversions of 0.1, 0.5 and 0.9 respectively, were determined.

The position parameter $\tau_{0.1}=10^3/T_{0.1}$ as well as the shape parameters $\Delta=10^3(1/T_{0.1}-1/T_{0.5})$ and $\nabla=(1/T_{0.5}-1/T_{0.9})/(1/T_{0.1}-1/T_{0.9})$ were calculated. By using the nomogram [13], the kinetic parameters given in Table 6 were obtained in two iteration cycles for two dehydration processes and for 9 other pyrolysis processes that we called 'deamination'.

No correlation can be observed between the structure of the complex and the apparent kinetic parameters, viz. the reaction order n, the activation energy E and the pre-exponential factor A, but generally, with increasing E, log$A$ also increases, which may be considered to be a kinetic compensation effect.

We tested the non-linear compensation law by means of Eq. (5). The 'theoretical' pre-exponential factor values, logA', are given in the last column of Table 6. Obviously, the log$A$ and logA' values are practically identical. In order to characterize this equality, we performed a logA' *vs.* log$A$ linear regression and calculated the parameters of the equation

Table 6 Kinetic parameters derived from the TG curves

Compound	Stage	$\tau_{0.1}$	n	E/kJ	log$A$	logA'
I.	b	2.2883	1.66	329.95	37.04	37.05
II.	b	2.2523	2.37	342.55	37.94	37.92
III.	a	3.0075	0.41	49.1	4.70	4.75
	b	2.1413	0.63	253.47	25.86	25.79
IV.	b	2.1367	2.15	370.54	38.95	38.96
V.	b	2.1552	0.30	230.53	23.36	23.36
VI.	b	1.9048	–0.28	694.46	66.98	66.88
VII.	b	2.2075	0.10	161.83	16.00	15.93
VIII.	a	2.7027	1.65	112.35	13.13	13.15
	b	1.4859	0.07	64.26	1.47	1.51
IX.	b	1.3106	1.57	124.37	5.15	5.22

a – dehydration; b – 'deamination'

$$\log A' = m\log A + n$$

The parameters are as follows:

$$m = 0.9981 \text{ and } n = 0.0407$$

with a correlation coefficient equal to r=0.9999979.

This means an excellent agreement, since the absolute equality corresponds to m=1, n=0 and r=1

In conclusion, Eq. (5) describes very well the correlation between A, E, $\tau_{0.1}$ and q.

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