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KINETIC ANALYSIS OF THERMOGRAVIMETRIC DATA. XVIII. THERMAL DECOMPOSITION OF SOME [Co(AMINE)$_2$ (NCS)$_2$] TYPE COMPLEXES

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ABSTRACT

[Co(*p*-toluidine)$_2$(NCS)$_2$] (I), [Co(*m*-toluidine)$_2$(NCS)$_2$] (II) and [Co(aniline)$_2$(NCS)$_2$] (III) have been synthesized. Kinetic parameters n, E and Z (apparent reaction order, activation energy and pre-exponential factor) have been derived from the TG curves recorded under 12 different working conditions. The influence of the sample weight (m_0) and of the heating rate (q) upon the kinetic parameters as well as upon the decomposition temperature and the amount of amine liberated in the first decomposition stage are discussed. Mean values of the activation energy and of the decomposition temperature are discussed in terms of the Co—amine bond strength and molecular structure based on IR evidence.

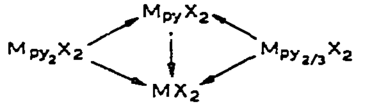
INTRODUCTION

The [Co(amine)$_2$X$_2$] type complex compounds with amine = aromatic or heterocyclic amines and X = pseudohalides (NCO$^-$, NCS$^-$ or NCSe$^-$) are easily formed by the interaction of CoX$_2$ and of the corresponding amine in aqueous solutions and especially in anhydrous solvents (e.g. ethanol, acetone, amyl alcohol).

In the literature the synthesis and characterization of some derivatives of this type have been reported, viz. with amine = urotropine [1], thiazole [2], benzidine, phenylhydrazine [3], quinoleine [4], *o*-toluidine [5], triaminotriethylamine [6] and aniline [7]. The majority of the above-mentioned complexes are thiocyanato derivatives and the number of the analogous cyanato- and seleno-cyanato complexes is very reduced.

The thermal decomposition of these complexes has not been studied. The derivatographic study of [Co(pyridine)$_4$ (NCS)$_2$] showed the thermal decomposition of this complex to lead to the formation of the not very stable intermediate [Co(pyridine)$_2$(NCS)$_2$], which loses the pyridine molecules in two relatively distinct stages [8—10] (through the [Co(pyridine)(NCS)$_2$] intermediate).

For the thermal decomposition of [M(pyridine)$_2$X$_2$] type complexes [M = Ni(II), Co(II), Mn(II), Zn(II), Cd(II), Cu(II) and X = halides or pseudohalides] various reaction schemes have been evidenced [10—17]. The possible reaction paths can be summarized as follows



In our previous papers [18—21] the thermal decomposition of [Co(amine)$_2$X$_2$] type complexes, with amine = aromatic amines and X = Cl, Br and I, has been studied both in isothermal and dynamic temperature conditions. The kinetic parameters n, E and Z, which will be referred to as reaction order, activation energy and pre-exponential factor, have been derived and the influence of the working conditions such as sample weight and heating rate has been studied. Although a part of our results seems to be consistent with the formation of a [Co(amine)$_{2/3}$X$_2$] relatively stable type intermediate, the position of the end of weight loss after the first deamination stage depends very much on the working conditions, viz. increasing both heating rate and sample weight leads to the diminution of the fraction of amine liberated up to the end of weight loss. As far as the derived kinetic parameters are concerned, they showed a systematic variation with working conditions.

In the present paper a thermogravimetric (TG) study of the following complexes has been made: [Co(p-toluidine)$_2$(NCS)$_2$] (I), [Co(m-toluidine)$_2$(NCS)$_2$] (II) and Co(aniline)$_2$(NCS)$_2$] (III).

TG MEASUREMENTS AND DERIVATION OF THE KINETIC PARAMETERS

In order to study the influence of the initial sample weight (m_0) and heating rate (q) upon the thermal decomposition of complexes (I)—(III), the TG curves have been recorded under 12 different working conditions, by using 25, 50, 75 and 100 mg samples and by performing heating rates of 5, 10 and 15 K min^{-1}. Some representative TG curves are presented in Fig. 1. The sample weight corresponding to Co(NCS)$_2$ is marked by a horizontal dashed line.

As seen from Fig. 1, the first stage of the decomposition leads to the formation of Co(NCS)$_2$, i.e to the loss of both amine molecules in the case of curves a, but the end of weight loss appears much earlier with curves b. At the same time the shape of the TG curves is modified by the working conditions and also a shift of the TG curves in parallel with the temperature axis can be observed. The influence of working conditions is shown by the data presented in Table 1, containing the number of amine molecules (X) liberated up to the end of weight loss and the position parameter (τ) of the TG curves defined in our previous paper [22] as $\tau = \nu_{0.1} = 10^3/T_{0.1}$, where T_α stands for the absolute temperature corresponding to the conversion α (in this case α = 0.1), by considering $\alpha = 1$ at the end of weight loss.

Table 1 shows a systematic variation (decrease) of X with both increasing sample weight and heating rate. Thus an end to weight loss on the TG curve never indicates the formation of a well-defined intermediate corresponding

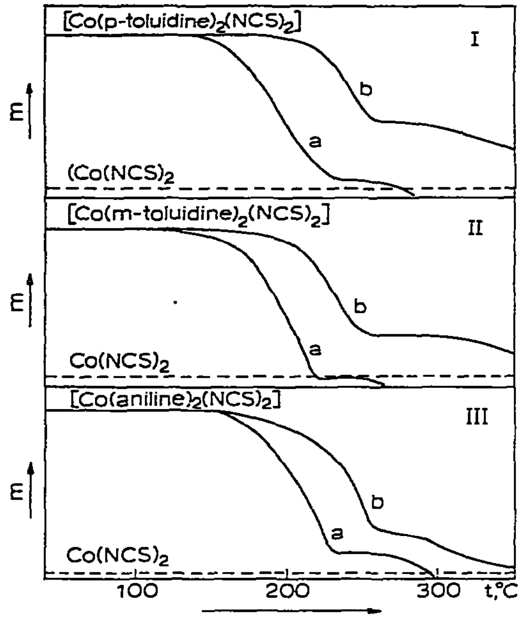


Fig. 1. Typical TG curves of the complexes (I), (II) and (III). a, m_0 = 25 mg; q = 5 K min^{-1}. b, m_0 = 100 mg, q = 15 K min^{-1}.

to the composition given by the position of the plateau. There can be working conditions leading to the end of weight loss before the integral formation of the relatively stable intermediate. A similar effect has also been observed in our earlier papers [18,19], Table 1 also shows decreasing τ values, i.e. the shift of the $T_{0.1}$ "decomposition temperature" towards higher values, with increase of both sample weight and heating rate.

TABLE 1

Number of amine molecules liberated (X) during the first decomposition stage and the position parameter τ

Heating rate (K min^{-1})	Sample weight (mg)	I		II		III	
		X	τ	X	τ	X	τ
5	25	1.91	2.309	2.03	2.283	2.05	2.244
	50	1.66	2.270	1.78	2.244	1.96	2.189
	75	1.40	2.244	1.53	2.213	1.84	2.195
	100	1.25	2.183	1.44	2.213	1.77	2.171
10	25	1.91	2.306	2.03	2.276	1.94	2.207
	50	1.64	2.230	1.66	2.213	1.87	2.143
	75	1.35	2.219	1.48	2.207	1.84	2.188
	100	1.19	2.207	1.43	2.159	1.75	2.169
15	25	1.91	2.276	1.91	2.250	1.96	2.188
	50	1.54	2.183	1.65	2.125	1.96	2.136
	75	1.28	2.159	1.48	2.183	1.82	2.131
	100	1.18	2.125	1.34	2.159	1.75	2.116

TABLE 2

Kinetic parameters of the first decomposition stage

Heating rate (K $\min^{-1}$)	Sample weight (mg)	I			II			III		
		n	*E* (kJ mole^{-1})	log *Z*	*n*	*E* (kJ mole^{-1})	log *Z*	*n*	*E* (kJ mole^{-1})	log *Z*
5	25	1.56	109	9.3	1.00	129	11.6	0.70	100	8.2
	50	1.00	106	9.1	0.86	92.9	7.4	0.48	103	8.6
	75	0.70	106	9.0	0.12	70.3	4.6	0.23	84.2	6.2
	100	0.27	98.4	7.8	−0.52	67.0	4.6	0.14	77.5	5.5
10	25	1.31	88.7	7.5	0.66	101	8.8	0.64	95.1	7.6
	50	0.89	86.5	7.0	0.37	92.9	7.4	0.61	84.2	6.9
	75	0.53	84.6	6.3	−0.62	67.8	4.6	0.30	61.1	3.8
	100	0.19	81.1	6.2	−0.70	64.0	4.4	0.17	48.1	2.1
15	25	1.25	78.2	6.4	0.50	88.7	7.7	0.61	82.1	6.6
	50	0.84	77.8	6.0	0.08	89.2	7.4	0.36	90.8	7.3
	75	0.42	72.5	5.2	−0.64	63.1	3.9	−0.12	65.2	4.1
	100	−0.12	68.3	4.9	−0.86	60.7	3.9	−0.72	50.1	2.5

Although the de-amination does not occur entirely in the first stage of the thermal decomposition, an attempt has been made to derive kinetic parameters n, E and Z from the first portion of the TG curve (up to the first end of weight loss). For this purpose the authors' computerized integral method has been used (proposed as "method 3" in our previous paper [23]). This method has been preferred to methods 1 and 2 on the basis of the results obtained [24]. The very high values of Jaffé's correlation coefficient ($\rho > 0.99$) shows that this first stage of the TG curve can be very well characterized by means of the kinetic parameters. Table 2 contains the kinetic parameters derived (Z is expressed in s^{-1})

INFLUENCE OF WORKING CONDITIONS

Since the thermal decomposition is sensitive to both sample weight and heating rate, mean values have been calculated separately for each sample weight and heating rate used, in order to obtain a clear picture of these influences. The mean values of X and τ are presented in Table 3.

It is obvious that the number of amine molecules liberated up to the end of weight loss decreases clearly with increasing sample weight. A similar, but no so important, effect can be observed with increasing heating rate. These results give no evidence for the formation of either a [Co(amine)$(NCS)_2$] or a [$Co(amine)_{2/3}(NCS)_2$] type intermediate and suggest the idea that the thermolysis yields $Co(NCS)_2$ directly, but an end to relative weight loss appears due to the limitation of the amine evolution rate, presumably the diffusion of the gaseous products towards the air phase is hindered. This effect becomes more important at higher sample weights and at lower temperatures. The latter could explain why the end of weight loss appears earlier with (I) and (II), as compared to (III), having a higher decomposition temperature. Table 3 shows the mean X values to increase in the order (I), (II) and (III), but the mean τ values decrease in the same order, in agreement with the above hypothesis.

Decreasing τ values with increasing sample weight also indicate a limitation of the decomposition rate. The similar effect of increasing heating rate

TABLE 3

Mean values of the amine molecules liberated and the position parameter

Working conditions		I		II		III	
		X	τ	X	τ	X	τ
m_0 (mg) =	25	1.91	2.297	1.99	2.270	1.98	2.213
	50	1.61	2.227	1.70	2.194	1.93	2.156
	75	1.34	2.207	1.50	2.201	1.83	2.171
	100	1.21	2.172	1.40	2.177	1.76	2.152
q (K min^{-1}) =	5	1.55	2.252	1.70	2.238	1.90	2.200
	10	1.52	2.240	1.65	2.214	1.85	2.169
	15	1.48	2.186	1.59	2.179	1.87	2.143

TABLE 4

Mean values of the kinetic parameters for different sample weights and heating rates

Working conditions	I			II			III		
	n	E (kJ mole^{-1})	log Z	n	E (kJ mole^{-1})	log Z	n	E (kJ mole^{-1})	log Z
m_0 (mg) = 25	1.37	92.0	7.7	0.72	106.2	9.4	0.65	92.4	7.3
50	0.91	90.1	7.4	0.44	91.6	7.4	0.48	92.6	7.6
75	0.55	87.7	6.8	−0.38	67.1	4.4	0.14	70.2	4.7
100	0.11	82.6	6.3	−0.69	63.9	4.3	−0.14	58.6	3.4
q (K min^{-1}) = 5	0.88	104.8	8.8	0.36	90.0	7.1	0.39	90.5	7.1
10	0.75	85.4	6.7	−0.07	81.4	6.3	0.43	72.1	5.1
15	0.60	74.2	5.6	−0.23	75.4	5.7	0.03	72.0	5.2

is not relevant in this respect, since a shift of the TG curves towards higher temperatures also occurs with "theoretical" curves [25]. The mean values of the kinetic parameters are given in Table 4.

As seen from Table 4, a clear decreasing tendency of all the kinetic parameters can be observed with increase of both sample weight and heating rate. This effect consequently appears with compounds (I) and (II) and only a few exceptions can be found in the the case of (III). Similar effects have been reported by other authors with respect to the apparent activation energy [26—28] and in our earlier papers with respect to both E and Z [29,30]. .

This effect seems to be connected to the same limitations of the diffusion rate, as mentioned above, and presumably also to the limitation of the heat transfer. A limitation of the decomposition rate by an effect, which becomes more important at higher heating rates or sample weights, makes the TG curves flatter (the temperature interval of the thermal decomposition becomes larger). In terms of kinetic parameters, this means [25] a lower activation energy E. If this effect becomes more important in an earlier stage of the decomposition step (at $\alpha < 0.5$), the shape parameter ∇, defined by us [22] as

$$\nabla = \frac{\nu_{0.5} - \nu_{0.9}}{\nu_{0.1} - \nu_{0.9}}$$

might decrease, which in terms of kinetic parameters means a decrease of the n value. If this effect becomes important only later (at $\alpha > 0.5$), the ∇ parameter increases, as well as the apparent reaction order. Such an increase of n with increasing heating rate has been observed with the de-amination of some $[Co(diox.H)_2(amine)_2]X$ type complexes (diox.H_2 stands for an α-dione dioxime, X for halide or pseudohalide) giving well-defined intermediates and corresponding plateaux of the TG curves.

In our case a very important decrease of n is observed with increasing heating rate and sample weight, even leading to negative n values, i.e. the above-mentioned limitations can be presumed to appear at $\alpha < 0.5$. It is worth mentioning that our earlier hypothesis concerning the existence of two distinct kinetic stages of the first decomposition stage of $[Co(amine)_2X_2]$ type complexes [18,19] could also be a consequence of such a negative reaction order. Since in these papers [18,19] a Coats—Redfern linearization [32] has been performed, by presuming six n values corresponding to $0 \leqslant n \leqslant 2$, for an experimental TG curve corresponding to a negative n value no straight line could be obtained, but a "linearization" corresponding to a higher n value than the real one, may sometimes suggest the curve obtained to be formed from two intersecting straight lines, with a lower activation energy in the first "kinetic" stage and with a higher one in the second stage, exactly as found by us earlier.

GENERAL MEAN VALUES OF THE KINETIC PARAMETERS AND THE KINETIC COMPENSATION EFFECT

Since in the present paper the thermal decomposition reactions have been studied under the same 12 working conditions, it seems legitimate to com-

TABLE 5

General mean values of the kinetic parameters, the position parameter and the kinetic compensation parameters

Compound	n	E (kJ $mole^{-1}$)	log Z	τ	a'	a	b	σ
I	0.74	88.1	7.0	2.226	0.1163	0.1073	−2.39	−0.170
II	0.02	82.3	6.4	2.210	0.1155	0.1169	−3.25	−0.069
III	0.28	78.2	5.8	2.171	0.1135	0.1174	−3.43	0.000

pare the general mean values, calculated from all individual values presented in Table 2. Results are given in Table 5.

As seen, the activation energy decreases in the order (I) > (II) > (III), exactly as the nucleophilic character of the corresponding amines, reflected by Hammett's σ constant of the substituent of the aniline [39] given in Table 5. This means that the apparent activation energy varies in parallel with the strength of the Co—amine bond to be broken. This means that the apparent activation energy has some real physical meaning correlated to the chemical process if TG curves are recorded in well standardized working conditions and for closely analogous decomposition reactions.

The mean values of E and log Z, as well as their individual values presented in Table 2, vary in parallel. Generally, for a given reaction, these parameters are correlated by a

$$\log Z = aE + b$$

type kinetic compensation law [29,30]

This relation is perfectly verified by the E and log Z values reported in the present paper, as shown by the high values found for Jaffé's correlation coefficient ($\rho > 0.99$) by means of the least-squares method. The kinetic compensation parameters a and b are given in Table 5.

As regards the meaning of the compensation parameter a, we presumed it to be even more directly correlated to the strength of the bond to be broken than the activation energy, viz. the higher the bond strength the lower the a parameter will be [33]. Garn [34] presumes it to be correlated to a certain decomposition temperature T_c. By taking $10^3/\tau$ for T_c, Garn's compensation parameter becomes

$$a' = \frac{\tau \log e}{R} \times 10^{-3}$$

In our earlier papers [24,35—37] the a' values have been found to be very close to the experimental a values. Nevertheless, these results, seemingly consistent with Garn's hypothesis, were not relevant enough, since the activation energy frequently varies in the same direction as the decomposition temperature, e.g. if a single ligand is varied in $[Co(diox.H)_2(amine)_2]X$ or $[Co(en)_2(amine)X]Y_2$ type complexes [24,36,37] ("en" = ethylenediamine).

Garn's compensation parameter a', as defined above, is given in Table 5 for the complexes studied. Obviously, the a' values vary in exactly the opposite direction than the *a* values. This behaviour is in contradiction to Garn's hypothesis, but is in agreement with ours.

As seen from the mean *E* and τ values, in the case of the complexes studied, the higher the activation energy the lower the decomposition temperature. This apparently anomalous behaviour might be related to the molecular structure. In the $[Co(diox.H)_2(amine)_2]X$ and $[Co(en)_2(amine)X]Y_2$ type complexes the amine ligand enters in the composition of bulky complex ions and the presence and position of the CH_3 substituents of the amine molecule can be presumed not to essentially modify the crystal lattice. In the case of the complexes studied, the situation is completely different. According to IR and magnetic susceptibility measurements the analogous $[Copy_2(NCS)_2]$ complex has a distorted octahedral structure with NCS bridges [38]. For the terminal NCS ligands of $[Copy_4(NCS)_2]$ the C=N valence vibration band is situated at 2074 cm^{-1} and that of C—S at 805 cm^{-1}. The same bands appear at 2100 and 790 cm^{-1}, respectively, in the case of the NCS bridges of $[Copy_2(NCS)_2]$ [38]. Since the IR spectra of our complexes show these bands to be situated at 2120 cm^{-1} and 790 cm^{-1}, respectively, these values can be taken as evidence of a similar octahedral structure. Thus, although the CH_3 substituent would strengthen the Co—amine bond, it might reduce the stability of the crystal lattice by steric hindrance.

Thus, the a' parameter defined by means of the decomposition temperature decreases in the order (I) > (II) > (III), but the experimental compensation parameter increases in the same order (I) < (II) < (III), in agreement with our hypothesis, since the mean activation energy, which might be presumed to be correlated to the Co—amine bond strength, decreases in the above order.

Generally, the values of *a* and a' are very close to each other, which apparently pleads for Garn's hypothesis, i.e. the compensation parameter *a* seems to depend mainly on a certain decomposition temperature. But under well-standardized working conditions and in the case of compounds of related structure, the decomposition temperature depends to an important degree on the strength of the bond to be broken and the difference between Garn's and our hypothesis becomes unimportant. In such cases TG data do not allow a choice between the two hypotheses. Our results presented in Table 5 seem to be important in this respect, since they are not consistent with both hypotheses, but only with ours.

EXPERIMENTAL

*Synthesis of [Co(aniline)$_2$(NCS)$_2$], [Co(*m*-toluidine)$_2$(NCS)$_2$] and [Co(*p*-toluidine)$_2$(NCS)$_2$]*

0.1 Mole cobalt(II) acetate and 0.2 mole KCNS were dissolved in 300 ml hot water. The solution was kept boiling and treated with 0.1 mole aniline (*m*- and *p*-toluidine) in a few ml of alcohol. After 15—20 min boiling the solution is cooled and the formed crystalline products are filtered, washed with water and dried in air (yield 60—70%).

Analysis

$[Co(aniline)_2(NCS)_2]$ (M. Wt. calcd. 361.3), reddish violet prisms. Co cald. 16.31, found 16.25; NCS calcd. 32.15, found 31.88.

$[Co(m\text{-toluidine})_2(NCS)_2]$ (M. Wt. calcd. 389.4), reddish violet needles. Co calcd. 15.14, found 15.19, NCS calcd. 30.04, found 29.77.

$[Co(p\text{-toluidine})_2(NCS)_2]$ (M. Wt. calcd. 389.4) reddish-violet prisms. Co calcd. 15.14, found 15.03; NCS calcd. 30.04, found 30.15. (Cobalt was determined complexometrically and thiocyan as $BaSO_4$).

IR spectra were recorded by means of a UR 20 Carl Zeiss Jena recording spectrophotometer in KBr pellets. The Co—N (amine) bondings have a strongly covalent character (N—H: 3225 s, 3265 s, 3160 s; NH_2: 1620 m, NH_2 820 s cm^{-1}).

The thermal decomposition of the complexes has been investigated in the presence of static air by means of a thermobalance constructed on the basis of literature data [40]. A platinum crucible has been used as sample holder.

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