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KINETIC ANALYSIS OF THERMOGRAVIMETRIC DATA XVI

THERMAL DECOMPOSITION OF SOME COMPLEXES OF THE TYPE $[Co(niox \cdot H)_2(amine)_2]X$

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The influence of the sample weight and the heating rate upon the thermal deamination of $[Co(niox \cdot H)_2(pyridine)_2]I$ (I), $[Co(niox \cdot H)_2(aniline)_2]I$ (II) and $[Co(niox \cdot H)_2(pyridine)_2]$ NCS $\cdot$ 1.5 H_2O (III) and upon the dehydration of (III) has been studied (niox $\cdot$ H_2 stands for nioxime: 1,2-cyclohexanedione dioxime). Kinetic parameters n, E and Z have been derived by means of the authors' three computerized integral methods. Analysis of the results shows method 1 to be equivalent to method 2 with respect to the numerical values obtained, but it needs a tenfold computer time. Method 3 gives better results due to the better choice of input data. The influence of the working conditions and of the chemical constitution upon the kinetic parameters, as well as the kinetic compensation effect, are discussed.

The stepwise thermal decomposition of complexes $[Co(diox.H)_2(amine)_2]X$ (diox.H_2 stands for an α-dione dioxime, and X for the outer sphere anion) has been studied under dynamic temperature conditions in our earlier papers [1, 2]. If the amine is an aromatic amine or a pyridine base and X a halide or pseudohalide anion. The first weight loss stop on the TG curve frequently corresponds to the loss of an amine molecule, i.e. to the substitution of this amine by the outer sphere anion and to the formation of a non-electrolytic complex:

$$[Co(diox.H)_2(amine)_2]X \rightarrow [Co(diox.H)_2(amine)X] + amine. \qquad (1)$$

For these de-amination reactions the apparent kinetic parameters n, E and Z, which will be referred to as reaction order, activation energy and pre-exponential factor, respectively, have been derived and the dependence of these parameters both on the working conditions (sample weight m_0, heating rate q) and on the chemical composition (nature of diox.H_2, amine and X) has been observed.

In the present paper the influence of the sample weight and of the heating rate has been studied in the case of the following complex salts: $[Co(niox.H)_2(pyridine)_2]I$ (I), $[Co(niox.H)_2\text{-}(aniline)_2]I$ (II), $[Co(niox.H)_2(pyridine)_2]NCS \cdot 1.5\ H_2O$ (III) and $[Co(niox.H)_2(aniline)_2]NCS$ (IV) (where niox.H_2 stands for 1,2-cyclohexanedione dioxime (nioxime)).

Details of the synthesis of these complexes, as well as the characterization of some new binary salts of the corresponding cations, are given in the experimental part.

The second aim of this paper is to test and to compare the three computerized integral methods proposed in our previous paper [3].

Deriving of kinetic parameters

In our TG measurements, performed at constant heating rate, the actual weight values m_i have been determined at equal time intervals. Some representative TG curves are given in Fig. 1 for the complexes I–III.

As seen from these curves, the first stage in the thermal decomposition is clearly the above-mentioned substitution reaction for [Co(niox.H)$_2$(pyridine)$_2$]I and [Co(niox.H)$_2$ · (aniline)$_2$]I (curves *a* and *b*), i.e. a well-defined plateau appears at the weight values corresponding to the non-electrolytic products.

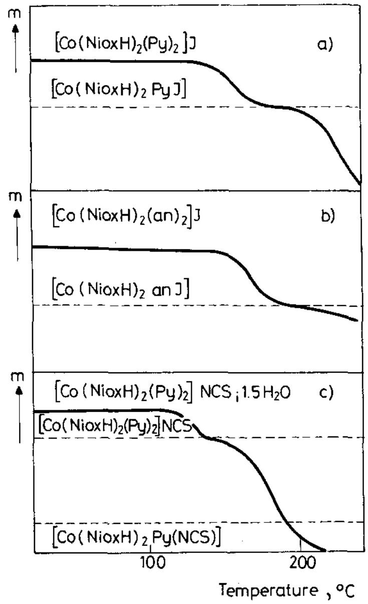

Fig. 1. Typical TG curves of the compounds studied. (*Py* stands for pyridine, *an* for aniline) *a* — $m_0 = 25$ mg, $q = 5°$/min, *b* — $m_0 = 25$ mg, $q = 10°$/min, *c* — $m_0 = 75$ mg, $q = 5°$/min

The thermal decomposition of [Co(niox.H)$_2$(pyridine)$_2$]NCS · 1.5 H_2O presents completely different features. The dehydration begins at a surprisingly high temperature (over 110°) and occurs rapidly in a narrow temperature interval. Its end is not marked by a plateau; only an inflexion point can be observed. The substitution reaction does not lead to a stable intermediate either. At the weight corresponding to the presumed non-electrolytic product, not even an inflexion appears; only a marked change in the slope can be seen, which shows the superposition of further decomposition processes on the substitution reaction.

Some TG curves of compound IV are given in Fig. 2. The horizontal dashed lines denoted by "1" represent the weight of the sample corresponding to the loss of one, and that denoted by "2" to the loss of two aniline molecules.

The shapes of the TG curves are seen to be strongly affected by the working conditions (controlled and uncontrolled ones). Curve *a* might be consistent with the formation of the presumed intermediate, but in curves *b* and *c* there is no evidence of the substitution reaction [1]. Obviously, these TG curves cannot be used for kinetic analysis purposes.

As far as the calculation methods are concerned [3]:

In method 1 the input data are: the heating rate (q), the initial and the final sample weights (m_0 and m_1) corresponding to the thermal decomposition stage, as well as the experimental sample weight (m_i) and temperature (t_i,°) pairs. The computer performs a double minimization of the standard deviation by varying n and E, and calculates the exponential integral by means of the authors' approximation formula.

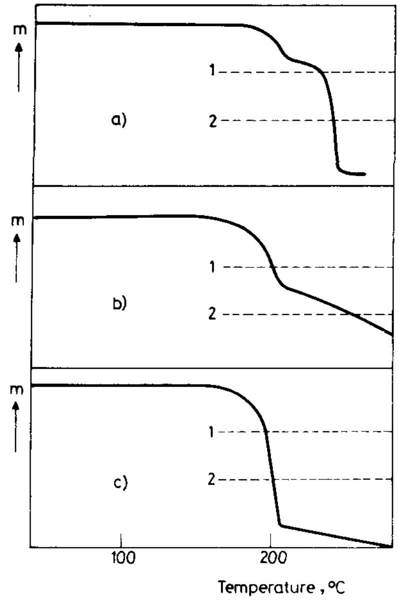

Fig. 2. Typical TG curves of [Co(niox · H)$_2$(aniline)$_2$]NCS. a — $m_0 = 100$ mg, $q = 15°/\mathrm{min}$; b — $m_0 = 25$ mg, $q = 10°/\mathrm{min}$; c — $m_0 = 100$ mg, $q = 5°/\mathrm{min}$

In method 2 the same input data are used, but this method is based on the Coats–Redfern linearization. The computer calculates the slope of the straight line corresponding to the maximum value of Jaffé's correlation coefficient, by varying n.

In method 3 the same calculation principle is applied as in method 2, but the input data are different. By plotting m_i *vs.* temperature and by tracing the most probable TG curve, nine $\vartheta_\alpha = 10^3/T_\alpha$ values are determined graphically, corresponding to the conversion (transformation degree) values $\alpha = 0.1, 0.2, 0.3, \ldots,$

0.9 (T_α stands for the absolute temperature corresponding to the conversion α). These ϑ_α values, as well as the heating rate, are fed into the computer.

Calculations gave very low relative standard deviations ($\delta_{\min} < 10^{-4}$) and very high correlation coefficient values ($\varrho > 0.99$). This means that the individual TG curves can be characterized excellently by means of the kinetic parameters n, E and Z.

Result are presented in Tables 1 – 3 (Z is given in s^{-1}).

It is obvious that the kinetic parameter values derived by means of methods 1 and 2 are practically identical, although these methods are based on two different approximations of the exponential integral, method 1 being more correct from a mathematical point of view. These results show the very wide possibilities of the Coats – Redfern method and indicate the equivalency of method 1 and 2 as far as the numerical values obtained are concerned. On the other hand, due to the double minimization performed in method 1, the computer time is about tenfold as compared to method 2. Thus, our first conclusion is that it is not worth using method 1, although it seems to be more correct, because the same values can be derived in a shorter time by using method 2.

Influence of working conditions

The data presented in Tables 1 – 3 show the decreasing tendency of both E and log Z with increasing sample weight and also with increasing heating rate. As regards the apparent reaction order values, they are rather scattered and no conclusion can be drawn at first sight.

In order to obtain a clear picture of the influence of the working conditions upon the kinetic parameters and to have a possibility of comparing the efficiency of

Table 1

Kinetic parameters of thermal deamination of $[Co(niox.H)_2(pyridine)_2]I$ derived by means of methods 1, 2, and 3

Heating rate, °/min	Sample, weight, mg	n			E, kJ/mol			log Z		
		1	2	3	1	2	3	1	2	3
5	25	1.30	1.29	1.19	154	154	141	16.7	16.8	15.0
	50	0.92	0.92	0.81	148	147	140	15.7	15.8	14.7
	75	0.98	0.98	0.98	143	142	136	15.2	15.2	14.4
	100	1.08	1.08	1.00	133	132	125	14.0	14.1	13.0
10	25	1.17	1.17	1.05	127	125	118	13.4	13.7	12.4
	50	0.83	0.83	0.78	104	103	99	10.5	10.7	10.0
	75	0.85	0.84	0.80	107	106	104	10.7	11.0	10.4
	100	0.97	0.97	0.92	104	103	99	10.3	10.4	9.7
15	25	1.24	1.24	1.04	104	102	80	10.7	10.8	7.7
	50	0.92	0.92	0.89	87	86	85	8.5	8.4	8.3
	75	0.93	0.93	0.81	85	84	73	8.3	8.6	6.7
	100	0.87	0.87	0.79	69	68	64	5.9	6.1	5.4

method 3 with the other two methods, a statistical analysis of the data obtained has been performed. For this purpose, mean values of the kinetic parameters have been calculated, separately for each sample weight and for each heating rate. Since methods 1 and 2 give the same mean values, these are presented together in a single column. The mean values obtained are listed in Table 3.

In this Table a systematic decrease of both E and $\log Z$ can be observed with increasing sample weight and with increasing heating rate, without exception. It is worth mentioning that in Tables 1–3 one can observe 9–10 inversions of this order for each method; these inversions are eliminated by means of this statistical analysis. At the same time, there are several cases when methods 1 and 2 give very close values for different sample weights, but method 3 ensures a clearer separation of them.

A similar effect of decreasing activation energy with increasing heating rate has been observed by other authors, too [4–7]. Decreasing activation energy with increasing heating rate and with increasing sample weight has been reported in our previous papers concerning the thermal decomposition of other types of complexes [8, 9]. The explanation of this effect, which means simply that, with increasing sample weight and heating rate, the temperature interval corresponding to the thermal decomposition increases, could be the limitation of the heat transfer and/or of the diffusion rate of the gaseous product evolved.

The influence of the working conditions upon the apparent reaction order is not quite clear. Methods 1 and 2 give a rigorously valid systematic variation of n with sample weight in a single case, *viz.* for the deamination of (III), where n decreases with increasing sample weight and even becomes negative. This is easy to understand, since with larger sample weights the temperature interval of the

Table 2

Kinetic parameters of thermal deamination of [Co(niox.H)$_2$(aniline)$_2$]I derived by means of methods 1, 2 and 3

Heating rate, °/min	Sample weight, mg	n			E, kJ/mol			$\log Z$		
		1	2	3	1	2	3	1	2	3
5	25	0.66	0.66	0.62	224	223	233	24.5	24.6	26.0
	50	0.45	0.45	0.59	218	217	216	24.0	24.3	23.6
	75	0.08	0.03	0.08	198	196	203	21.5	21.3	22.1
	100	0.09	0.06	0.33	193	194	180	20.9	21.0	19.1
10	25	0.95	0.95	0.95	218	217	227	24.0	24.2	25.3
	50	0.47	0.47	0.56	205	202	207	22.5	22.3	22.9
	75	0.44	0.39	0.65	164	163	175	17.6	17.9	20.3
	100	0.52	0.53	0.35	163	161	151	17.2	17.4	15.7
15	25	0.70	0.72	0.66	142	141	158	14.9	15.0	16.9
	50	0.83	0.84	0.31	142	140	141	15.0	14.9	14.8
	75	0.34	0.37	0.52	146	144	146	15.3	15.2	15.4
	100	0.50	0.50	0.23	135	135	128	13.6	13.6	12.8

Table 3

Kinetic parameters of thermal dehydration and deamination of [Co(niox.H)$_2$(pyridine)$_2$] NCS, 1.5 H_2O derived by means of methods 1, 2 and 3

	Heating rate, °/min	Sample weight, mg	n			E, kJ/mol			log Z		
			1	2	3	1	2	3	1	2	3
Dehydration	5	25	1.72	1.72	1.48	320	321	317	40.6	40.6	39.7
		50	0.95	0.95	0.91	277	277	303	34.5	34.4	37.7
		75	0.74	0.75	0.56	254	253	276	31.7	31.8	34.4
		100	0.67	0.67	0.58	246	247	231	30.7	30.9	29.1
	10	25	1.09	1.05	1.48	266	271	283	33.2	33.5	35.5
		50	0.50	0.48	1.31	275	276	273	34.5	34.2	34.0
		75	1.16	1.17	1.67	250	253	248	32.0	32.2	30.6
		100	1.47	1.47	1.88	243	246	231	30.0	30.4	28.9
	15	25	1.64	1.64	1.37	244	245	249	30.0	30.1	31.0
		50	0.84	0.83	1.36	261	261	235	32.7	33.0	29.1
		75	1.02	1.04	0.72	228	227	250	27.9	28.1	31.4
		100	0.97	0.96	1.17	230	231	236	28.5	28.6	29.4
Deamination	5	25	0.94	0.94	0.81	176	176	158	18.3	18.0	15.8
		50	0.83	0.83	0.86	174	174	176	18.0	17.9	18.2
		75	0.50	0.51	0.55	156	155	164	16.0	15.9	16.7
		100	0.42	0.41	0.34	142	140	131	14.3	14.2	13.0
	10	25	0.73	0.73	0.70	159	160	162	16.5	16.2	16.5
		50	0.17	0.17	0.20	156	158	163	15.9	16.0	16.6
		75	0.01	0.02	0.12	132	130	120	13.1	12.8	11.6
		100	−0.17	−0.17	−0.20	96	97	78	8.7	8.6	6.3
	15	25	0.64	0.62	0.56	155	156	145	15.9	15.8	14.5
		50	0.89	0.87	0.75	126	122	117	12.0	11.7	11.0
		75	−0.03	−0.03	−0.12	113	111	106	10.7	10.5	9.8
		100	−0.23	−0.22	−0.89	116	118	86	11.1	11.4	7.3

decomposition becomes more extended and the probability of the superposition of further decomposition stages increases; the slope of the TG curves decreases more slowly in this terminal region of the decomposition stage, which in terms o kinetic parameters means the decrease of n. In other two cases (deamination of (I) and (II), methods 1 and 2 also show a decreasing tendency of n with increasing m_0, but a slight inversion is observed with each reaction. From the data concerning the dehydration of (III) no conclusion can be drawn.

Method 3 gives a much clearer picture in this respect. 15 of the 16 mean values indicate the decreasing of n with increasing m_0; only for the dehydration of (III) in the 100 mg sample has a higher n value than expected been obtained.

The influence of the heating rate on the reaction order is more obscure. Method 3 suggests that it decreases with increasing heating rate. This is clearly expressed in two cases [deamination of (I) and (III)] and with the other two reactions n has

Table 4

Mean values of the kinetic parameters obtained for the same sample weight and heating rate values by means of methods 1, 2 and 3

Reaction	working conditions	*n*		*E*, kJ/mol		log *Z*	
		1, 2	3	1, 2	3	1, 2	3
Deamination of $[Co(niox.H)_2(Py)_2]I$	m_0 = 25 mg	1.24	1.04	128	113	13.7	11.7
	m_0 = 50 mg	0.92	0.89	112	108	11.6	11.0
	m_0 = 75 mg	0.93	0.81	111	105	11.5	10.5
	m_0 = 100 mg	0.87	0.79	102	96	10.2	9.4
	q = 5°/min	1.07	1.00	144	136	15.4	14.3
	q = 10°/min	0.95	0.89	110	105	11.3	10.6
	q = 15°/min	0.95	0.77	86	76	8.4	7.0
Deamination of $[Co(niox.H)_2(an)_2]I$	m_0 = 25 mg	0.77	0.74	194	206	21.2	22.7
	m_0 = 50 mg	0.58	0.49	187	189	20.5	20.5
	m_0 = 75 mg	0.28	0.42	169	175	18.2	19.2
	m_0 = 100 mg	0.36	0.30	164	153	17.3	15.9
	q = 5°/min	0.32	0.40	208	208	22.7	22.7
	q = 10°/min	0.59	0.63	186	190	20.3	21.0
	q = 15°/min	0.61	0.43	141	143	14.7	15.0
Dehydration of $[Co(niox.H)_2(Py)_2]$. NCS . 1.5 H_2O	m_0 = 25 mg	1.48	1.44	278	283	34.6	35.4
	m_0 = 50 mg	0.76	1.19	271	270	33.9	33.6
	m_0 = 75 mg	0.98	0.98	244	258	30.6	32.1
	m_0 = 100 mg	1.04	1.21	241	233	29.9	29.1
	q = 5°/min	1.02	0.88	274	282	34.4	35.2
	q = 10°/min	1.05	1.58	260	259	32.5	32.2
	q = 15°/min	1.12	1.15	241	243	29.9	30.2
Deamination of $[Co(niox.H)_2(Py)_2]$ . . NCS	m_0 = 25 mg	0.77	0.69	164	155	16.8	15.6
	m_0 = 50 mg	0.63	0.60	152	152	15.3	15.3
	m_0 = 75 mg	0.17	0.18	133	130	13.2	12.7
	m_0 = 100 mg	0.01	−0.25	118	99	11.4	8.7
	q = 5°/min	0.67	0.64	162	157	16.5	15.9
	q = 10°/min	0.19	0.20	136	131	13.4	12.7
	q = 15°/min	0.32	0.07	127	113	12.4	10.7

a higher value for q = 10°/min than for q = 15°/min. Methods 1 and 2 also show such a decreasing tendency in the deamination of (I), but in the deamination of (II) and the dehydration of (III) a slight but systematic increase is observed.

At any rate, when the above considerations are taken into account method 3 seems to give a more unified picture of the influence of the working conditions and in our view this method is to be preferred. Its superiority seems to be due to the better choice of the input data. In the case of method 2 the actual experimental weight data are affected by accidental errors; in addition their distribution along the TG curve is not uniform, since in the recording of sample weight values at equal time intervals, one has more experimental points at the beginning of the thermal decomposition, rate of the decomposition being lower in this portion, and very few points of the TG curve corresponding to the rapid decomposition. In method 3, by tracing the most probable TG curve on the basis of the same experimental points, the accidental errors are partially eliminated and by taking the above-mentioned nine ϑ_α values, the uniform distribution of the points used is automatically ensured.

General mean values of the kinetic parameters and the kinetic compensation effect

Since the above-mentioned four thermal decomposition reactions have each been studied under the same 12 working conditions, it seems justified to compare the general mean values of the kinetic parameters. These general mean values, calculated from the kinetic parameter values presented in Tables 1 – 3, obtained for all working conditions used and by means of all three methods, are given in Table 5.

From the mean reaction order values no conclusion can be drawn.

The mean activation energy values show clear individual characteristics and seem to have some real physical meaning. The much higher value obtained for (II) as compared to (I) might be related to the higher strength of the Co-aniline bond as compared to the Co-pyridine one.

The influence of the outer sphere anion can be seen if one compares the deamination of (I) with the corresponding reaction of (III). The lower activation energy obtained for (I), as well as the lower decomposition temperature, show clearly the high labilizing effect of the I^- anion upon the coordinated amine molecules, similarly as observed with other cobalt complexes [9].

The very high activation energy obtained for the dehydration of (III) indicates very strongly bonded water molecules. Generally, the activation energies of similar

Table 5

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

Reaction	n	E, kJ/mol	log Z	τ	a' mol/kJ	a mol/kJ	b
Deamination of $[Co(niox.H)_2(pyridine)_2]I$	0.95	111	11.4	2.455	0.125	0.123	−2.16
Deamination of $[Co(niox.H)_2(aniline)_2]I$	0.50	178	19.4	2.357	0.123	0.121	−2.37
Dehydration of $[Co(niox.H)_2(pyridine)_2]$ . . NCS . 1.5 H_2O	1.11	259	32.3	2.562	0.134	0.130	−1.42
Deamination of $[Co(niox.H)_2(pyridine)_2]NCS$	0.36	139	13.8	2.285	0.119	0.120	−2.93

dehydration reactions of complexes under similar working conditions do not exceed 120 – 130 kJ/mole. The uncommon behaviour of this crystallization water is also indicated by the high decomposition temperature. The behaviour of (IV) seems to be in agreement with the general picture given above. Since reaction (1) begins at higher temperature if I is substituted by NCS (compounds (I) and (III)), or if pyridine is substituted by aniline (compounds (I) and (II)), it must be shifted to even higher temperature in the case of compound (IV), exactly as observed in Fig. 3. At such a high temperature, reaction (1) does not take place alone; other decomposition reactions occur at the same time. This is why the shape of the TG curve is very sensitive to the working conditions and does not allow a kinetic analysis.

Since the decomposition temperatures do not result directly from the kinetic parameters given in Tables 1 – 3, the mean value of the position parameter τ, proposed in our previous paper [10] and defined as $\tau = \vartheta_{0.1}$, is also given in Table 5. It is obvious that the decomposition temperature ($10^3/\tau$ can be taken as a kind of standard decomposition temperature) cannot be directly correlated to the activation energy, even if analogous chemical reactions are concerned. If one compares the deaminations of (I) and (II) (having the same outer sphere anion), or of (I) and (III) (having the same amine to be replaced), it is obvious that the higher the activation energy, the higher the decomposition temperature. However, a similar relation is not valid for the deaminations of (II) and (III), where both the outer sphere anions and the amines to be replaced are different.

The mean values of log Z, as well as its individual values given in Tables 1 – 3, vary in parallel. Generally, for a given reaction these magnitudes are correlated by a kinetic compensation law of the type

$$\log Z = aE + b$$

as reported in our earlier papers [1, 9, 11, 12]. We presumed the compensation parameter a to be even more directly correlated to the strength of the bond to be broken than the activation energy [13]. Garn [14] assumes that it depends on a certain decomposition temperature (T_C) according to the relation $a = \dfrac{\log e}{RT_C}$.

The E and log Z values verify the above compensation law excellently, as shown by the high values obtained for Jaffé's correlation coefficient ($\varrho > 0.99$). The kinetic compensation parameters derived from all data presented in Tables 1 – 3 by means of the least squares method are given in Table 5, together with Garn's parameter calculated as $a' = \dfrac{\tau \log e}{R} \times 10^{-3}$ by using the mean τ values of Table 5 and by expressing R in kJ/Kmole, in order to have a' in mole/kJ, as for a obtained from the compensation law. The a and a' values are seen to be very close to each other, which seems to be consistent with Garn's hypothesis.

Table 6

Characterization of some complexes of the type [Co(niox.H)$_2$(amine)$_2$]X

Amine	*X*	Mol. weight calcd.	Aspect	Analysis		
				Calcd.		Found
Aniline	Br	607.4	brown prisms	Co Br	9.70 13.16	9.55 13.08
Aniline	I	654.4	thin brown acicular cryst.	Co N	9.04 12.85	9.01 12.60
Aniline	NCS	585.6	yellow-brown short prisms	Co N	10.07 16.75	9.89 16.66
Aniline	ClO_4	627	yellow-brown microcryst.	Co	9.40	9.36
Pyridine	Br	579.4	brown prisms	Co Br	10.17 14.11	10.22 14.23
Pyridine	I	626.4	brown plates	Co I	9.41 20.26	9.32 20.32
Pyridine	NCS. 1.5 H_2O	584.6	yellow-brown prisms	Co NCS	10.08 9.93	9.89 9.78
Pyridine	ClO_4	598.9	yellow microcryst.	Co	9.98	9.77

Experimental

Synthesis of [*Co*(*niox.H*)$_2$(*pyridine*)$_2$]*X and* [*Co*(*niox.H*$_2$)(*aniline*)$_2$]*X*

20 mmole cobalt(II) acetate, 40 mmole (5.6 g) nioxime and 60 mmole pyridine (aniline) were dissolved in 300 ml 75% methanol. The mixtures were oxidized by air bubbling during 3–4 hours. The dark brown solutions formed were filtered. One third portions of the parent solutions were treated with 20 g KBr, 20 g KI and 15 g KCNS, respectively, dissolved in 100 ml water.

The separated crystalline products were filtered off, washed with cold water and dried in air. Their characterization is given in Table 6.

The thermal decomposition of the complexes was investigated in the presence of air by means of a thermobalance constructed on the basis of literature data [15]. 25, 50, 75 and 100 mg samples were used in a platinum crucible. The constant heating rates were 5, 10 and 15°/min.

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Résumé — On a étudié l'influence du poids de l'échantillon et de la vitesse de chauffage sur la désamination thermique de [Co(niox · $H)_2$(pyridine$)_2$]I (I), [Co(niox · $H)_2$(aniline$)_2$]I (II) et [Co(niox · $H)_2$(pyridine$)_2$]NCS · 1.5 H_2O (III) ainsi que sur la déshydratation de (III) (niox · H_2 représente la nioxime: 1,2-cyclohexanedione dioxime). A l'aide des trois méthodes d'intégration sur ordinateur des auteurs, les paramètres cinétiques *n*, *E* et *Z* ont pu être déduits. L'analyse des résultats montre que la méthode est équivalente à la méthode 2 quant aux valeurs numériques obtenues; elle exige cependant dix fois plus de temps d'ordinateur. La méthode 3 donne de meilleurs résultats en raison de la meilleure sélection des données d'entrée. On discute l'influence des conditions de travail et de la structure chimique sur les paramètres cinétiques ainsi que l'effet de compensation cinétique.

Zusammenfassung — Der Einfluss des Probengewichts und der Aufheizgeschwindigkeit auf die thermische Desaminierung von [Co(niox · $H)_2$(pyridin$)_2$]I (I), [Co(niox · $H)_2$(anilin$)_2$]I (II) und [Co(niox · $H)_2$(pyridin$)_2$]NCS · 1.5 H_2O (III) sowie auf die Dehydratisierung von (III) wurde untersucht (niox · H_2 bedeutet Nioxim: 1,2-cyclohexandion-dioxim). Die kinetischen Parameter *n*, *E* und *Z* wurden mit Hilfe der drei komputerisierten Integralmethoden der Autoren abgeleitet. Die Analyse der Ergebnisse zeigt, daß Methode 1 der Methode 2 hinsichtlich der erhaltenen numerischen Werte ebenbürtig ist, doch eine zehnfache Rechenzeit beansprucht. Methode 3 ergibt bessere Resultate dank der besseren Wahl der eingegebenen Daten. Der Einfluss der Arbeutsbedingungen und der chemischen Struktur auf die kinetischen Parameter, sowie der kinetische Kompensationseffekt werden diskutiert.

Резюме — Изучено влияние веса образца и скорости нагрева на термическое деаминирование комплексов [Co(ниокс.H$)_2$ (пиридин$)_2$] I (I), [Co(ниокс.H$)_2$ (анилин$)_2$] I (II) и [Co(ниокс.H$)_2$ (пиридин$)_2$] NCS. 1.5 H_2O (III), где (ниокс.H$)_2$ — ниоксим: диоксим 1.2-циклогександиона. Для последнего из указанных соединений изучена также дегидратация. С помощью трех интегральных, вычислительных методов, предложенных авторами, вычислены кинетические параметры *n*, *E* и *Z*. Анализ результатов показал, что метод 1 эквивалентный методу 2 в отношении полученных числовых значений, но требует в десять раз больше машинного времени. Метод 3 дает лучшие результаты, что обусловлено лучшим подбором вводных данных. Обсуждено влияние экспериментальных условий и химического состава соединений на кинетические параметры, совместно с кинетическим компенсационным эффектом.