

Special Reviews

KINETICS AND MECHANISM OF SUBSTITUTION REACTIONS OF COMPLEXES, XX

INFLUENCE OF HEATING RATE ON THE THERMAL DECOMPOSITION OF [Co(DH)₂(amine)₂]NCS TYPE COMPLEXES AS INVESTIGATED BY THERMOGRAVIMETRY

J. ZSAKÓ, E. KÉKEDY and Cs. VÁRHELYI

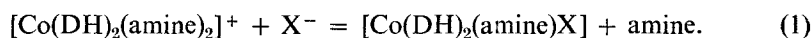
Faculty of Chemistry, Babeş-Bolyai University, Cluj, Rumania

(Received May 22, 1969)

Thermal decomposition of 21 complexes of the type [Co(DH)₂(amine)₂]NCS has been studied under the conditions of thermogravimetric analysis, by using different heating rates. From the thermogravimetric curves apparent kinetic parameters of the pyrolysis reaction have been derived by means of the modified Doyle method. Apparent reaction order increases and apparent activation energy decreases with increasing heating rate. Thus, the obtained kinetic parameters do not characterize the purely chemical reaction, but the complex heterogeneous process as a whole. The explanation of the observed effect is discussed. Results are compared with those obtained with other analogous complexes.

In our previous papers [1–3] the thermal decomposition of [Co(DH)₂(amine)₂]X was studied under the conditions of thermogravimetric analysis, by using a single heating rate. In the above formula DH₂ stands for a molecule of dimethylglyoxime.

Our investigations showed the first stage of the pyrolysis to be a substitution reaction according to the following equation:



Thus, one of the amine molecules in the internal co-ordination sphere is substituted for an anion from the external sphere, a relatively stable intermediate is formed and the liberated amine is volatilized.

For the kinetic study of this reaction Horowitz and Metzger's method [4] was used. Since this method is not very accurate [5], in our further investigations the modified Doyle method has been used, as described in our previous paper [5]. By means of this method the pyrolysis of the analogous bis-diphenylglyoximate-diamino-cobalt(III) complexes [Co(DH)₂(amine)₂]X has been studied [6, 7].

For deriving kinetic parameters from thermogravimetric curves another integral method has been proposed by Ozawa [8]. This method is based on the application of different heating rates and kinetic parameters, since the reaction order n , activation energy E_a and pre-exponential factor Z of the Arrhenius

equation are presumed to be independent of the heating rate q . If these parameters are the same regardless of the heating rate, the modification of the heating rate produces only a nearly parallel shift of the thermogravimetric curve [9] and this shift depends in fact upon the activation energy of the process [10].

Our experiments concerning the influence of the heating rate showed in the case of the iodides $[\text{Co}(\text{DH})_2(\text{amine})_2]\text{I}$ that the apparent activation energy decreases with increasing heating rate [11]; this means that Ozawa's method cannot be used.

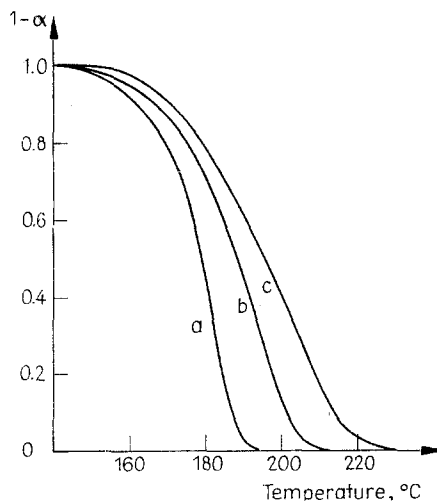


Fig. 1. Thermogravimetric curves of $[\text{Co}(\text{DH})_2(\text{p-toluidine})_2]\text{NCS}$ at different heating rates. (a) $q = 5\text{ }^\circ\text{C/min}$; (b) $q = 10\text{ }^\circ\text{C/min}$; (c) $q = 15\text{ }^\circ\text{C/min}$

In the present paper thermogravimetric curves have been recorded for the analogous thiocyanato-complexes, by using different heating rates, namely 5, 10 and $15^\circ/\text{min}$. Experimental results are illustrated in Fig. 1, which contains thermogravimetric curves of $[\text{Co}(\text{DH})_2(\text{p-toluidine})_2]\text{NCS}$, recorded at different heating rates. As seen from this Figure, the curve is shifted and its shape is modified too; the increase of heating rate reduces the slope of the curve.

Thus, from these curves only apparent kinetic parameters can be derived and their values must depend upon the heating rate. Ozawa's method can be applied neither in the case of the iodides nor in the case of the thermal decomposition of the thiocyanates of these complex cations. On the other hand, the modified Doyle method enables us to derive kinetic parameters separately for each heating rate.

The basic relation used in the modified Doyle method is as follows [5]:

$$B = \lg \frac{ZE_a}{Rq} = \lg g(\alpha) - \lg p(x) \quad (2)$$

where R stands for the general gas constant; the functions $g(\alpha)$ and $p(x)$ have the following meaning:

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} \quad \text{and} \quad p(x) = - \int_{\infty}^x \frac{e^{-x}}{x^2} dx \quad (3)$$

where α stands for the decomposition degree of the initial compound and $f(\alpha)$ expresses the kinetic law of the decomposition under isothermal conditions, according to the equation:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (4)$$

where k stands for the rate constant. In the integral function $p(x)$ the variable x stands for the fraction E_a/RT . Numerical values of $-\lg p(x)$ have been listed in our previous paper [5] as a function of both temperature and activation energy E_a .

In Eq. (2) the magnitude of B depends only upon the nature of the pyrolysis process, but in the case of a given thermogravimetric curve it must have the same value for each point of the curve. The modified Doyle method is based on the constancy of B .

From the thermogravimetric curves the degree of decomposition can be calculated for each experimental point, according to the following relationship:

$$\alpha = \frac{W_0 - W}{W_0 - W_t} \quad (5)$$

where W , W_0 and W_t stand for the actual, initial and final weight of the sample, respectively.

Concerning the shape of the function $f(\alpha)$, functions of the following type are most frequently presumed:

$$f(\alpha) = (1 - \alpha)^n \quad (6)$$

where n stands for the apparent reaction order. By using the α values given by Eq. (5), the function $g(\alpha)$ can be calculated for each experimental point by presuming different reaction orders. The analytical shape of the function $g(\alpha)$ was given in our previous paper [5] for the following six reaction orders: 0, 1/3, 1/2, 2/3, 1 and 2. The table with the numerical values of $-\lg p(x)$ enables us to seek the E_a value which ensures the constancy of B during the thermal decomposition reaction. To find this E_a value easily, we gave a statistical criterion of the constancy of B . By using the $g(\alpha)$ values obtained for a given presumed reaction order n and the table of integrals, B values are calculated for each experimental point by presuming an approximate E_a value. These individual B values will be denoted by B_i . The arithmetic mean of these B_i values, denoted by \bar{B} , and the standard deviation of these individual B_i values from the arithmetic mean are calculated. The standard deviation, defined as

$$\alpha = \sqrt{\frac{\sum(B_i - B)^2}{r}} \quad (7)$$

where r stands for the number of experimental points, gives a quantitative characterization of the constancy of B and thus of the consistency of the presumed kinetic parameters with the experimental data.

The standard deviation δ is calculated for a given n and for various E_a values and its minimum indicates the best E_a value, that most consistent with the presumed reaction order. By repeating this trial-and-error procedure for other reaction orders too, the minimum δ values obtained can be compared, and it can be decided which gives the best reaction order, from those considered, as indicated by the minimum of these minimum δ values.

These calculations have been carried out for the above-mentioned six reaction orders. In the case of each thermogravimetric curve six $\lg g(\alpha)$ values have been calculated for each experimental point.

Table 1
 $\lg g(\alpha)$ values for the compounds (I) and (II) by presuming
 different reaction orders. Heating rate: $q = 10^\circ\text{C}/\text{min}$

Compound t °C	(1 - α)	$\lg g(\alpha)$ for the reaction orders						
		$n = 0$	$n = 1/3$	$n = 1/2$	$n = 2/3$	$n = 1$	$n = 2$	
(I)	160	0.9472	-1.278	-1.274	-1.271	-1.270	-1.266	-1.254
	170	0.8750	-0.903	-0.894	-0.889	-0.885	-0.875	-0.845
	180	0.7292	-0.567	-0.545	-0.534	-0.523	-0.499	-0.430
	190	0.4583	-0.266	-0.216	-0.189	-0.162	-0.107	-0.071
	200	0.1302	-0.060	0.047	0.107	0.170	0.309	0.826
(II)	130	0.9437	-1.250	-1.246	-1.243	-1.242	-1.238	-1.224
	140	0.8826	-0.931	-0.921	-0.916	-0.912	-0.903	-0.875
	150	0.7512	-0.603	-0.583	-0.573	-0.564	-0.543	-0.479
	160	0.6009	-0.399	-0.365	-0.347	-0.329	-0.293	-0.177
	170	0.3897	-0.215	-0.155	-0.124	-0.093	-0.026	0.194
	180	0.1268	-0.059	0.050	0.109	0.174	0.314	0.839

As an example, in Table 1 are given the fractions of the initial compound $(1 - \alpha)$ derived from experimental thermogravimetric curves, and the corresponding six $\lg g(\alpha)$ values, calculated by means of the formulae given in our previous paper [5]. These data are given for the following two compounds:



Further calculations have been carried out in the following way. For each reaction order the approximate activation energy has been estimated, by using

the $\lg g(\alpha)$ values and the integral table containing $\lg p(x)$ values. Thus, the variation of $\lg g(\alpha)$ in the case of compound (I), assuming $n = 0$, between 160 and 200° is 1.218 (see Table 1).

The variation of $\lg p(x)$ in the same temperature interval is 1.186 for $E_a = 26.0$ kcal/mole and 1.269 for 28.0 kcal/mole, respectively; i.e., the activation energy most consistent with the experimental data and with the presumed reaction order $n = 0$, must be approximately 27 kcal/mole. In order to determine more exactly this activation energy, $\lg p(x)$ values have been calculated in the indicated temperature interval for intermediate E_a values, namely for 26.2, 26.4 . . . 27.8 kcal/mole, by means of linear interpolation, by using the integral table given in our paper [5]. With the help of these interpolated values, individual B_i values have been calculated by using the five experimental $\lg g(\alpha)$ values for $n = 0$, separately for each E_a value. The arithmetic mean of the B_i values and the sums $\Sigma(B_i - \bar{B})^2$ have been calculated. The minimum of these sums indicates the best E_a value for the given reaction order.

In Table 2 these sums are given for several E_a values in the vicinity of their minimum. By comparing these minimum values obtained for different reaction

Table 2

The sums $\Sigma(B_i - \bar{B})^2$ calculated for the thermal decomposition of compounds (I) and (II) in the vicinity of their minimum value by presuming different reaction orders, together with the corresponding E_a values

Compound	n	E_a	$\Sigma(B_i - \bar{B})^2$	n	E_a	$\Sigma(B_i - \bar{B})^2$	n	E_a	$\Sigma(B_i - \bar{B})^2$
(I)	0	26.8	0.005878	1/3	29.0	0.001980	1/2	30.4	0.000583
		27.0	0.005667		29.2	0.001868		30.6	0.000523
		27.2	0.005803		29.4	0.001832		30.8	0.000521
			29.6		0.001951	31.0		0.000611	
	2/3	31.8	0.000097	1	34.6	0.002704	2	45.2	0.068514
		32.0	0.000033		34.8	0.002572		45.4	0.068262
32.2		0.000062	35.0		0.002595	45.6		0.068281	
		35.2	0.002643		45.8	0.068313			
(II)	0	18.0	0.014795	1/3	19.6	0.008744	1/2	20.4	0.006332
		18.2	0.014556		19.8	0.008478		20.6	0.006005
		18.4	0.014619		20.0	0.008484		20.8	0.006076
			20.2		0.008602				
	2/3	21.4	0.004385	1	23.6	0.004000	2	31.0	0.061246
		21.6	0.004096		23.8	0.003972		31.2	0.061171
21.8		0.004182	24.0		0.004148	31.4		0.061393	

orders, one can choose the best reaction order, that most consistent with experimental data. Thus, in the case of compound (I), the minimum of the sum $\Sigma(B_i - \bar{B})^2$ is the least for $n = 2/3$; in the case of compound (II) for $n = 1$. We can say that the pyrolysis of compound (I) is apparently of order $2/3$, with an activation energy of 32.0 kcal/mole; while that of compound (II) is apparently of first order, with an activation energy of 23.8 kcal/mole (see Table 2).

Similar calculations have been carried out for all the complexes studied. Results are given in Table 3.

This Table contains the best reaction order from the six tried: the corresponding activation energy; the standard deviation defined by relationship [7]; and the Z value calculated on the basis of the arithmetic mean B by using the obtained activation energy according to Eq. (2).

The same Table contains other reaction order values too, which have been obtained on the basis of the shape of the thermogravimetric curves. In our previous paper [10] a new method was given for determining the apparent reaction order. This method uses the magnitude

$$\nabla = \frac{\frac{1}{T_{0.5}} - \frac{1}{T_{0.1}}}{\frac{1}{T_{0.9}} - \frac{1}{T_{0.1}}} \quad (8)$$

where $T_{0.1}$, $T_{0.5}$ and $T_{0.9}$ stand for the absolute temperatures at which the fraction of the initial complex $(1 - \alpha)$ reaches the indicated 0.1, 0.5 and 0.9 values, respectively. This magnitude has been found to be an unequivocal function of the reaction order, according to the following relationship:

$$\nabla = 0.2670 + 0.125 n - 0.0048 n^2. \quad (9)$$

In Table 3, reaction orders obtained by means of relationship (9) are denoted by n_{∇} and those obtained with the help of the modified Doyle method are given as n_{δ} . By comparing the two sets of reaction order data one can observe quite a good agreement, similar to the case of the analogous iodides [11].

As regards the influence of heating rate on the kinetic parameters, a systematic variation of these parameters can be observed with increasing heating rate. Apparent reaction order generally increases with increasing heating rate. At the same time the apparent activation energy decreases in nearly all cases. A similar decrease of the activation energy with increasing heating rate has been observed by other authors too [12] in the thermal decomposition of PVC, and it has been reported in our previous paper [11] for the pyrolysis of bis-dimethylglyoximato-diamino-cobalt(III) iodides. The explanation of this effect is probably the following: A linear variation of the furnace temperature is ensured, but the real temperature of the sample is not the same as that of the furnace. The difference between the furnace temperature and the temperature of the sample depends upon the heating rate; it increases with increasing heating rate. Thus, the rate of

Table 3
Kinetic parameters of the thermal decomposition of $[\text{Co}(\text{DH})_2(\text{amine})_2]\text{NCS}$ type complexes at different heating rates

Amine	$q = 5^\circ\text{C}/\text{min}$				$q = 10^\circ\text{C}/\text{min}$				$q = 15^\circ\text{C}/\text{min}$						
	n_δ	$n\nabla$	E_a	$\lg Z$	δ	n_δ	$n\nabla$	E_a	$\lg Z$	δ	n_δ	$n\nabla$	E_a	$\lg Z$	δ
aniline	1	1.08	68.2	31.5	0.041	1	1.06	53.0	23.7	0.062	1	1.57	45.0	20.3	0.038
<i>o</i> -toluidine	1	0.89	35.8	17.8	0.026	1	1.33	24.1	10.7	0.015	1	0.77	22.6	10.3	0.037
<i>m</i> -toluidine	0	0.31	36.8	17.2	0.104	2/3	0.68	32.9	14.9	0.048	1	0.97	32.0	15.1	0.015
<i>p</i> -toluidine	1/3	0.34	35.0	15.7	0.016	2/3	0.85	32.0	13.0	0.003	1	1.15	25.8	10.7	0.024
<i>m</i> -xylydine	0	0.14	19.4	7.7	0.009	1/2	0.38	19.1	8.2	0.007	2/3	0.55	18.1	7.7	0.014
<i>o</i> -ethylaniline	0	0.17	25.8	10.0	0.007	1	1.50	23.5	9.9	0.014	1	0.19	21.6	7.8	0.013
<i>p</i> -ethylaniline	1	1.62	47.2	21.9	0.008	1/3	0.19	25.8	10.2	0.008	1/3	0.19	21.6	7.8	0.013
<i>p</i> -propylaniline	1	0.86	31.2	14.5	0.018	—	—	—	—	—	—	—	—	—	—
<i>o</i> -anisidine	1	0.17	31.9	12.7	0.049	1	1.03	24.4	10.2	0.040	1	1.11	22.8	10.1	0.011
<i>p</i> -anisidine	1/2	1.27	32.2	14.3	0.045	1/2	0.41	32.0	13.1	0.036	1/2	0.39	29.6	11.3	0.226
<i>o</i> -phenetidine	1	—	—	—	—	1	1.30	28.2	11.5	0.169	1	1.54	17.4	6.6	0.058
<i>p</i> -phenetidine	—	—	—	—	—	0	-0.05	16.4	5.0	0.052	1/3	0.17	16.0	5.5	0.023
<i>p</i> -Cl-aniline	1/2	0.45	32.2	14.6	0.015	1	0.84	23.8	9.8	0.026	1	0.90	21.6	9.0	0.014
<i>o</i> -Br-aniline	1/2	0.43	22.1	10.1	0.051	2/3	0.57	17.4	6.7	0.060	—	—	—	—	—
<i>m</i> -Br-aniline	2/3	0.67	26.8	11.7	0.017	2/3	0.72	23.2	11.0	0.031	1	0.87	19.4	7.8	0.017
<i>p</i> -Br-aniline	1/2	0.47	28.5	12.2	0.020	2/3	0.56	17.8	6.4	0.015	1/3	0.36	14.6	4.9	0.019
benzylamine	1	0.92	29.6	12.2	0.060	1	1.13	28.3	12.1	0.047	1	0.75	30.4	13.1	0.027
α -naphthylamine	1/2	0.56	14.4	3.9	0.014	0	0.02	17.2	5.2	0.022	—	—	—	—	—
pyridine	1	0.69	43.0	20.1	0.019	1	0.94	42.2	19.7	0.088	1	0.90	40.8	19.6	0.058
β -picoline	1	1.03	68.0	36.9	0.055	1	1.37	53.2	27.3	0.061	1	1.48	53.0	29.9	0.013
γ -picoline	2/3	0.60	42.0	17.8	0.024	2/3	0.69	34.2	14.5	0.017	2/3	0.69	26.5	10.3	0.036

decomposition is less than that corresponding to the furnace temperature and a reduced slope of the thermogravimetric curve results; this gives a higher reaction order and lower activation energy. On the other hand, the volatilization of the liberated amine is not instantaneous and a time-lag can appear between the liberation and the volatilization of the product; this also reduces the slope of the thermogravimetric curve. This effect is larger at higher heating rates and it can explain the observed phenomenon.

The $\lg Z$ values vary in parallel with activation energy, in the same manner as observed in our earlier experiments [6, 7, 11].

The results given above can be compared with those obtained for the analogous bis-diphenylglyoximato-complexes [7], studied at a single heating rate ($q = 10^\circ\text{C}/\text{min}$). In all cases the apparent activation energy is much higher in the case of dimethylglyoximato-complexes. By comparing the obtained activation energies with the activation energies derived for the analogous iodides, one can see that generally the activation energy of the thiocyanates is less than that of the iodides [11]. But this difference is not as clear as in the case of the diphenylglyoximato-complexes [7].

This difference is presumably due to the different activation energy of the purely chemical process.

The most important conclusion to be drawn from the obtained results is that the derived kinetic parameters do not characterize only the purely chemical process given by Eq. (1), but the complex pyrolysis process as a whole, involving besides the chemical reaction other processes too, such as heat transfer, diffusion, formation of crystallization centres, growth of these centres, volatilization of the product, etc. This is why all the apparent kinetic parameters are influenced by the heating rate, and $\lg Z$ varies in parallel with E_a .

Concerning the reproducibility of the results, it is worth mentioning that besides the heating rate, other working conditions have a quite considerable influence. By recording thermogravimetric curves for samples of the same weight (100 ± 0.3 mg in our experiments), and by using the same crucible a rather good reproducibility can be attained. The obtained activation energy values do not differ generally by more than 1–2 kcal/mole. This fact and the quite good agreement between the n_{∇} and n_{δ} values strongly suggests the possibility of characterizing thermogravimetric curves by means of the kinetic parameters n , E_a and Z , and of obtaining these data by means of the modified Doyle method. On the other hand, it is obvious that the physical meaning of these kinetic parameters is rather obscure.

Experimental

Synthesis of the studied complexes was performed by means of the method described earlier [3]. The purity of the compounds was controlled by analytical methods, by determining the cobalt and the sulphur content.

Two new compounds have been synthesized by means of the same method. Their characterization and analysis data are as follows:

[Co(DH)₂(p-chloraniline)₂]NCS (Mol. wt. 602.4)

brown prisms, Co calc. 9.78, Co found 9.83

S calc. 5.32, S found 5.45

[Co(DH)₂(p-propylaniline)₂]NCS (Mol. wt. 617.6)

brown needles, Co calc. 9.54, Co found 9.64

S calc. 5.19, S found 5.27

Thermogravimetric curves have been recorded by means of a thermobalance using a known procedure [13].

References

1. J. ZSAKÓ, Cs. VÁRHELYI and E. KÉKEDY, *Studia Univ. Babeş-Bolyai, Chem.*, 10 (2) (1965) 7.
2. J. ZSAKÓ, Cs. VÁRHELYI and E. KÉKEDY, *Analele Univ., Bucureşti, Ser. St. Nat.*, 14 (2) (1965) 15.
3. J. ZSAKÓ, Cs. VÁRHELYI and E. KÉKEDY, *J. Inorg. Nucl. Chem.*, 28 (1966) 2637.
4. H. H. HOROWITZ and G. METZGER, *Anal. Chem.*, 35 (1963) 1464.
5. J. ZSAKÓ, *J. Phys. Chem.*, 72 (1968) 2406.
6. J. ZSAKÓ, E. KÉKEDY and Cs. VÁRHELYI, *Studia Univ. Babeş-Bolyai, Chem.*, 14 (2) (1969) 117.
7. J. ZSAKÓ, Cs. VÁRHELYI and E. KÉKEDY, *J. Inorg. Nucl. Chem.*, in the press.
8. T. OZAWA, *Bull. Chem. Soc. Japan*, 38 (1965) 1881.
9. J. ZSAKÓ, *J. Chim. Phys.*, 66 (1969) 1041.
10. J. ZSAKÓ, *Revue roum. Chim.*, in the press.
11. J. ZSAKÓ, E. KÉKEDY and Cs. VÁRHELYI, *Revue roum. Chim.*, in the press.
12. D. FURNICA and I. A. SCHNEIDER, *Makromol. Chem.*, 108 (1967) 182.
13. L. ERDEY and F. PAULIK, *Magy. Tud. Akad. Kém. Oszt. Közl.*, 5 (1955) 461.
14. L. KÉKEDY, P. KRÖBL, Á. SZURKOS and E. KÉKEDY, *Studia Univ. Babeş-Bolyai, Chem.*, 3 (1958) 99.

RÉSUMÉ. — On a étudié par thermogravimétrie, avec différentes vitesses d'échauffement, la décomposition thermique de 21 complexes du type [Co(DH)₂(amine)₂]SCN. On a calculé suivant la méthode de DOYLE les paramètres cinétiques apparents déduits des courbes d'ATG. L'ordre apparent de la réaction augmente si la vitesse d'échauffement croît, alors que l'énergie d'activation apparente décroît. Les paramètres cinétiques obtenus ne caractérisent que le processus hétérogène complexe et non la réaction chimique proprement dite. Les effets observés ont été discutés et comparés avec les résultats obtenus avec d'autres complexes analogues.

ZUSAMMENFASSUNG. — Die thermische Zersetzung von 21 Komplexen des Typs [Co(DH)₂(Amin)₂]NCS wurde thermogravimetrisch bei verschiedenen Aufheizgeschwindigkeiten untersucht. Aus den TG-Kurven wurden die scheinbaren kinetischen Parameter der Reaktion mit Hilfe der Doyle'schen Methode ermittelt. Bei zunehmender Aufheizgeschwindigkeit wächst die scheinbare Reaktionsordnung während die scheinbare Aktivierungsenergie abnimmt. Die erhaltenen chemischen Parameter kennzeichnen nicht die eigentliche chemische Reaktion, sondern den ganzen komplexen heterogenen Vorgang. Die beobachteten Effekte wurden diskutiert und die Ergebnisse verglichen mit Resultaten von Untersuchungen anderer analoger Komplexe.

Резюме.— Исследован термораспад 21 комплекса типа $[\text{Co}(\text{DH})_2(\text{амин})_2]\text{NCS}$ в условиях термического анализа, при использовании разных скоростей нагрева. По термогравиметрической кривой рассчитаны кажущиеся кинетические параметры пиролитической реакции с помощью измененного метода Дойля. С увеличением скорости нагрева кажущийся порядок реакции увеличивается и кажущаяся энергия активации уменьшается. Таким образом, рассчитанные кинетические параметры не характеризуют исключительно химическую реакцию, а комплексный процесс в целом. В работе дискутируется наблюдаемый эффект. Результаты сравниваются с данными, полученными для подобных комплексов.