

THERMAL DECOMPOSITION KINETICS
OF DIETHYL DITHIOCARBAMATE COMPLEXES
OF COPPER(II) AND NICKEL(II)

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Thermogravimetric (TG), derivative thermogravimetric (DTG) and differential thermal analysis (DTA) curves of CuL_2 and NiL_2 ($\text{L}^- =$ diethyl dithiocarbamate anion) in air are studied. The main decomposition temperature ranges are: For CuL_2 , DTG 250–350°, DTA 300–320° and for NiL_2 , DTG 290–390°, DTA 360–400°. Mass loss considerations at the main decomposition stages indicate conversion of the complex to sulphides. Mathematical analysis of TG data shows that first order kinetics are applicable in both cases. Kinetic parameters (energy and entropy of activation and preexponential factor) are reported.

Transition metal dithiocarbamates have important technical applications, for example, as vulcanization accelerators, as fungicides, etc. As part of an investigation on the thermal decomposition of transition metal complexes [1], we have now studied the dithiocarbamate complexes. Thermoanalytical data (TG, DTG and DTA) of two typical complexes, i.e., diethyl dithiocarbamate complexes of copper(II) and nickel(II) are presented in this communication. Interpretation and mathematical analysis of these data and evaluation of order of reaction and the energy and entropy of activation, based on the differential method employing the Freeman–Carroll equation [2], the integral method using the Coats–Redfern equation [3] and the approximation method using the Horowitz–Metzger equation [4] are also given.

Experimental

Preparation of samples

Samples of diethyl dithiocarbamate copper(II) and diethyl dithiocarbamate nickel(II) [hereafter abbreviated as CuL_2 and NiL_2 respectively, where $\text{L}^- = (\text{C}_2\text{H}_5)_2\text{NCS}_2^-$] were prepared by adding, at room temperature (30°), 0.1 M aqueous solutions of copper(II) sulphate and nickel(II) sulphate respectively to 0.1 M solutions of sodium diethyl dithiocarbamate. An excess of the ligand was employed (molar ratio, ligand/metal = 4). The precipitates were filtered, washed thoroughly with water, then with alcohol and dried in a vacuum desiccator.

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BDH AR chemicals were used in the preparation. The purity of the samples was checked by elemental analysis for the metal and sulphur. CuL_2 requires Cu = 17.65%, S = 35.88%, found Cu = 17.60%, S = 35.40%. NiL_2 requires Ni = 16.60%, S = 36.37%; found Ni = 16.52%, S = 35.90%.

Apparatus

TG and DTA traces were recorded on a Stanton recording thermobalance Model TR 01 with a DTA attachment. The heating rates and other characteristics are given below: heating rate = 4°C min^{-1} , chart speed = 3 in. hr^{-1} , atmosphere-static air, crucible (DTA) platinum, reference substance Al_2O_3 .

X-ray powder patterns were taken on a Philips Debye-Scherrer camera with a diameter 5.73×10^{-2} m, employing Cu-K α radiation ($\lambda = 0.1542$ nm). I. R. spectra were recorded on a Carl-Zeiss UR-10 spectrophotometer.

Treatment of data

The instrumental TG traces were re-drawn as the mass vs temperature (TG) curves and also as the rate of loss of mass vs temperature (DTG) curves. The curves were drawn using standard curve sets. The instrumental DTA curves were used as such. The decomposition temperature ranges in DTG and DTA curves were noted and compared. Typical TG, DTG and DTA traces are presented in Figures 1 and 2.

The TG curves were studied in greater detail. The curves for CuL_2 and NiL_2 each exhibited a characteristic, well defined and non-overlapping first stage decomposition pattern. This is followed by subsequent minor oxidative decomposition

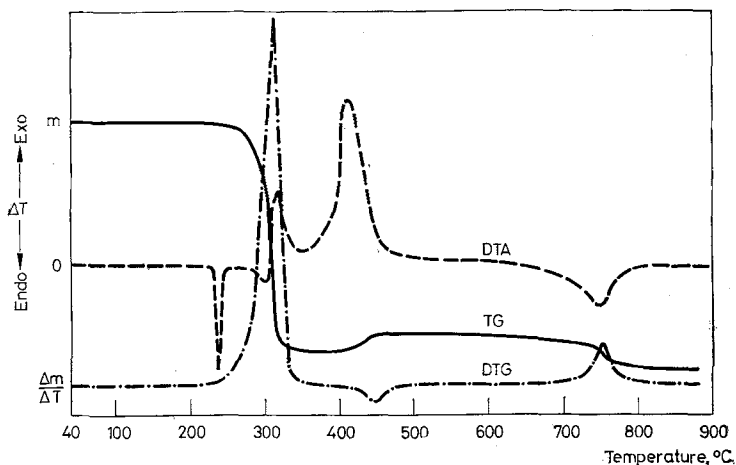


Fig. 1. TG, DTG and DTA traces of CuL_2

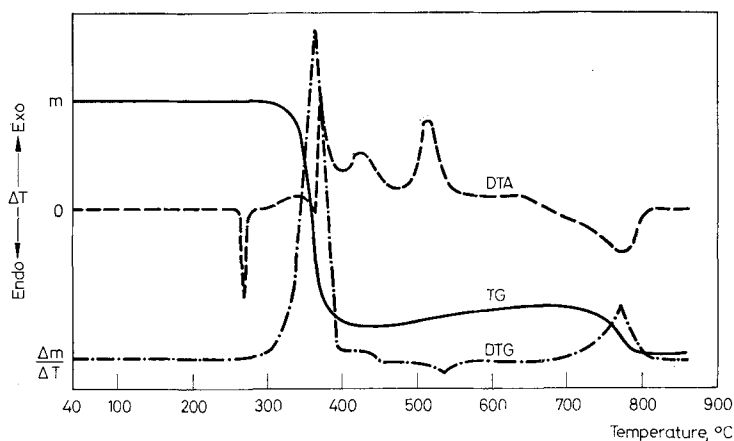


Fig. 2. TG, DTG and DTA traces of NiL_2

patterns. The first stage represents the major decomposition step in each case and mass loss considerations and X-ray diffraction data indicated the products to be $\text{Cu}_{1.8}\text{S}$ and NiS . The first stage was chosen for detailed study. For this purpose the relevant portion of the TG curve was re-drawn on an expanded scale, using standard curve sets. Three different methods were used to evaluate kinetic data from these TG traces.

The differential method using Freeman–Carroll equation [2]

The Freeman–Carroll equation was used in the form

$$\frac{\Delta \log(dw/dt)}{\Delta \log w_r} = \frac{(-E^*/2 \cdot 303R) \Delta(T^{-1})}{\Delta \log w_r} + n \quad (1)$$

where $w_r = w_\infty - w$; w_∞ = mass loss at the completion of the first stage reaction; w = mass loss up-to time t ; T = absolute temperature at time t ; n = order of reaction; R = gas constant in $\text{kJ deg}^{-1}\text{mole}^{-1}$ and E^* = energy of activation in kJ mole^{-1} . Of the above terms, w_r and T can be directly obtained from the TG traces. The mass-temperature gradient (dw/dT) could be obtained by drawing tangents, but a more accurate method, making use of Stirling's central difference formula for six points [5], was employed. The temperature slopes, dw/dT , were converted into time slopes dw/dt using the relation

$$(dw/dt) = (dw/dT)(dT/dt) = (dw/dT)\Phi \quad (2)$$

where Φ is the heating rate

A plot of $\frac{\Delta(T^{-1})}{\Delta \log w_r}$ versus $\frac{\Delta \log(dw/dt)}{\Delta \log w_r}$ was drawn and was found to be

linear. The order of reaction and activation energy (E^*) were obtained from the above graph.

The order (n) was found to be 0.9 for CuL_2 and 1.08 for NiL_2 . However, both CuL_2 and NiL_2 melt prior to decomposition and hence, n may be assumed to be unity. The usual first-order rate law expression

$$\left(\frac{dx}{dt}\right) = k(a - x) \quad (3)$$

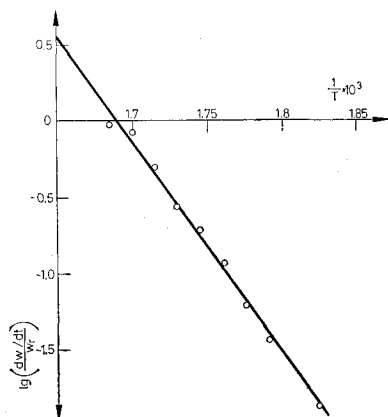


Fig. 3. Freeman-Carroll (modified) plot for CuL_2

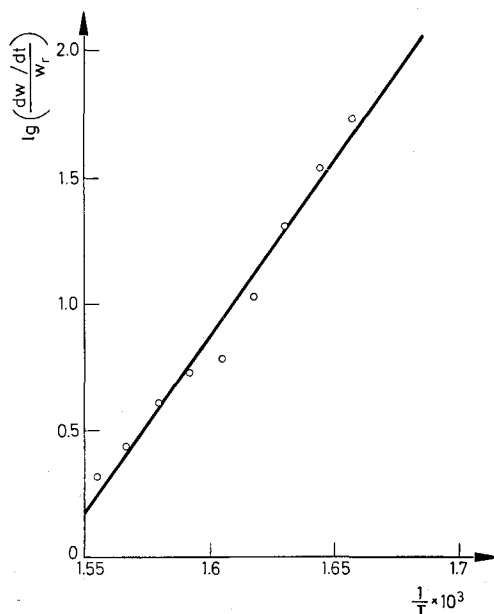


Fig. 4. Freeman-Carroll (modified) NiL_2

can be put into the following form using the terms w and w_r

$$(dw/dt) = kw_r \quad (4)$$

Combining this with Arrhenius equation, i.e.,

$$k = Z \exp(-E^*/RT) \quad (5)$$

$$\text{we get } \log [(dw/dt)/w_r] = \frac{-E^*}{2.303RT} + \log Z \quad (6)$$

A plot of the left hand side expression against (T^{-1}) was found to be linear, from the slope of which E^* was calculated. Z was calculated from the intercept and ΔS^* was obtained from the equation

$$Z = \frac{kT_s}{h} \exp(\Delta S^*/R) \quad (7)$$

where k is the Boltzmann constant and h is the Planck's constant. T_s is the temperature at the DTG peak. Typical curves concerning the applications of the Freeman–Carroll equation ($n = 1$) to CuL_2 and NiL_2 are given in Figures 3 and 4 respectively.

The integral method using the Coats–Redfern equation [3]

It was considered instructive to evaluate kinetic parameters using an integral method also, and for this the Coats–Redfern method was chosen [3]. For first-order processes, this equation may be written in the form

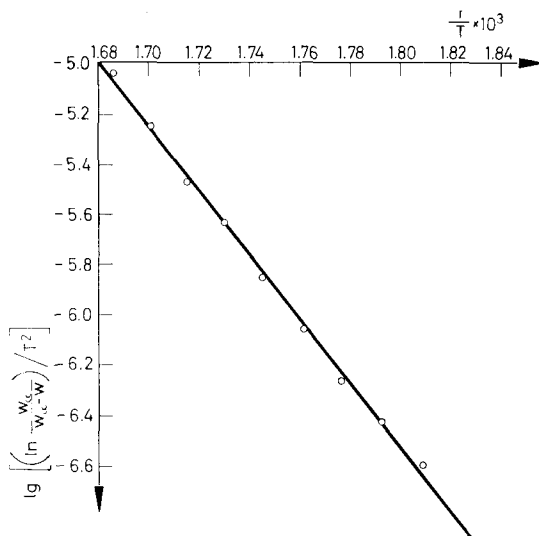
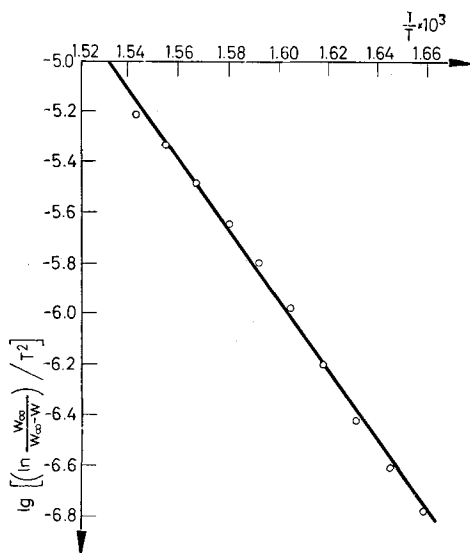


Fig. 5. Coats–Redfern plot for CuL_2

Fig. 6. Coats-Redfern plot for NiL_2

$$\log_{10} \left[\left(\log_e \frac{w_\infty}{w_\infty - w} \right) / T^2 \right] = \log_{10} \left[\frac{ZR}{\Phi E} \left(1 - \frac{2RT}{E^*} \right) \right] - E^*/2.303RT \quad (8)$$

Since $1 - 2RT/E^* \approx 1$, a plot of L. H. S. against $1/T$ was drawn (Figs 5 and 6), from the slope of which E^* was calculated. Using this value of E^* , Z was calculated from the intercept.

The approximation method using the Horowitz-Metzger equation [4]

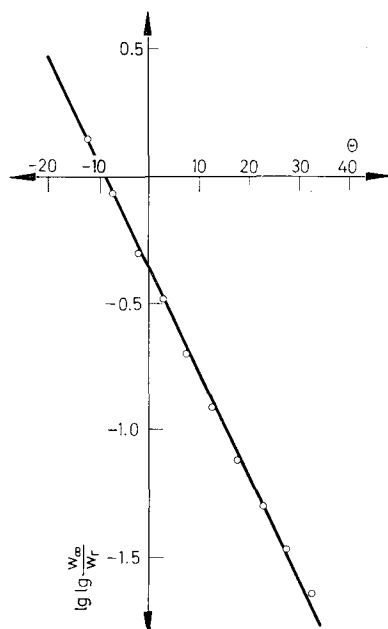
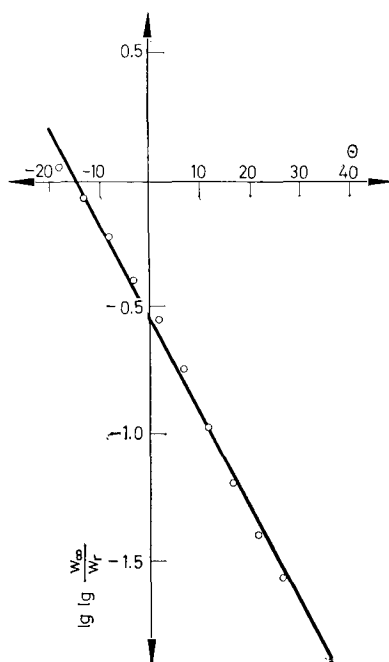
The Horowitz-Metzger equation, applicable to first order processes was employed. This equation is

$$\log \log \left(\frac{m_0 - m_f}{m - m_f} \right) = \frac{E^*\theta}{2.303RT_s^2} - \log 2.303 \quad (9)$$

where m_0 and m_f are the initial and final masses respectively and m is the mass at temperature T ; $\theta = T - T_s$ and the other terms have already been defined.

The above equation can be put in a different form, using the mass loss terms (w , w_r & w_∞) defined earlier in equation (1) i.e.,

$$\log \log (w_\infty/w_r) = \frac{E^*\theta}{2.303RT_s^2} - \log 2.303 \quad (10)$$

Fig. 7. Horowitz-Metzger plot for CuL₂Fig. 8. Horowitz-Metzger plot for NiL₂

A plot of $\log \log (w_\infty/w_r)$ versus θ was drawn and was found to be linear, from the slope of which E^* was calculated. Typical curves are given in Figs 7 and 8. The preexponential factor Z was calculated from the equation

$$\frac{E^*}{RT_s^2} = \frac{Z}{\Phi} nc_s^{n-1} \exp(-E^*/RT_s) \quad (11)$$

For the present case ($n = 1$), this reduces to

$$\frac{E^*}{RT_s^2} = \frac{Z}{\Phi} \exp\left(-\frac{E^*}{RT_s}\right) \quad (12)$$

The entropy of activation ΔS^* is calculated from the equation (7).

All the linear plots were drawn by the method of least squares and corresponding correlation coefficients (r) were also calculated.

Results and discussion

The decomposition temperature ranges in DTA and DTG, for both CuL_2 and NiL_2 , are given in Table 1. Data from independent pyrolytic experiments (carried out by heating in air weighed samples taken in porcelain crucibles) are also included in Table 1. Kinetic parameters calculated by employing the Freeman–Carroll, the Coats–Redfern and the Horowitz–Metzger equations are summarized in Table 2. The correlation coefficients (r) of the linear plots are also given in the appropriate tables. All the temperature values are given in $^\circ\text{C}$. X-ray diffraction data are presented in Table 3.

Thermal behaviour

Whilst it is true that the actual peak temperatures do not have much significance in view of their dependence on the sample mass etc., it is nevertheless useful to compare the DTG peaks with the DTA peaks, since we have used simultaneous TG-DTA. The DTG curve for CuL_2 gives 3 peaks as may be seen from Table 1. The very strong DTG peak at 308° corresponds closely to the exothermic DTA peak at 318° . This is a well-defined and non-overlapping peak. Mass loss at the end of this stage, read from the TG curve, is 70.7%. X-ray diffraction studies showed that the product at this stage is α -copper sulphide (Digenite) with the composition $\text{Cu}_{1.8}\text{S}$ (Table 3). The theoretical mass loss at this stage for the decomposition of $\text{CuL}_2 \rightarrow \text{Cu}_{1.8}\text{S}$ would be 77.4%, if we assume that the other decomposition products have completely volatilised off. Since the latter assumption is not completely correct, the discrepancy is justifiable. The DTG reverse peak at 430° (gain of mass) corresponds to the exothermic DTA peak at 417° . This could correspond to partial oxidation of $\text{Cu}_{1.8}\text{S}$ to CuSO_4 . The presence of sulphate at this stage was established by qualitative analysis and by i.r. spectra. Finally, the

Table 1
Thermal decomposition data

Substance	Peak temperatures in DTG, °C	Temperatures ranges in DTG, °C	Peak temperatures in DTA, °C	Temperature ranges in DTA, °C	% loss of mass			
					First stage		Final	
					From TG	**Theoretical	From TG	From independent pyrolysis
*CuL ₂	308 s	250–350	230 endo (m) (sh)	300–320	70.7	77.4	75.2	78.4
	430 w (br)	390–470	318 exo (m)	380–460				
	750 w	730–770	417 exo (s)	700–760				
*NiL ₂	357 s	290–390	260 endo (m) (sh)	360–400				
	510 w (br)	450–570	365 exo (m)	480–540	70.1	74.5	80.6	79.0
	770 w	710–810	510 exo (m)	750–810				

Abbreviations: s = strong; w = weak; m = medium; br = broad; sh = sharp; br = broad; sh = sharp; endo = endothermic; exo = exothermic.

* L = [(C₂H₅)₂NCS₂]

** Based on the assumption that the complexes have decomposed quantitatively to yield the sulphides, Cu_{1.8}S and NiS and that any other product has volatilized off.

§ Based on the assumption that the final products are the oxides CuO and NiO

Table 2
Kinetic data

Substance	Parameters	from Freeman— Carroll equation	from Coats— Redfern equation	from Horowitz— Metzger equation
CuL ₂ <i>m</i> = 54 mg <i>w</i> _∞ = 38.2 mg	<i>E</i> [*] , kJ mole ⁻¹	265.5	246.5	264.7
	<i>Z</i> , s ⁻¹	4.48 × 10 ²¹	9.87 × 10 ¹⁹	1.17 × 10 ²¹
	Δ <i>S</i> [*] , J mole ⁻¹ °K ⁻¹	164.1	131.9	153.0
	<i>r</i>	0.997	0.998	0.999
NiL ₂ <i>m</i> = 53.5 mg <i>w</i> _∞ = 37.5 mg	<i>E</i> [*] , kJ mole ⁻¹	263.2	261.6	282.3
	<i>Z</i> , s ⁻¹	2.28 × 10 ¹⁹	1.90 × 10 ¹⁹	1.50 × 10 ²¹
	Δ <i>S</i> [*] , J mole ⁻¹ °K ⁻¹	119.5	117.9	154.3
	<i>r</i>	0.988	0.998	0.996

Abbreviations: L = [C₂H₅)₂NCS₂]; *m* = mass of substance taken; *w*_∞ = total loss of mass for the particular decomposition stage; *r* = correlation coefficient of the linear plot.

Table 3
X-ray powder diffraction data

Substance	<i>d</i> -spacing (observed) Å	Intensity order (observed)	Substance	<i>d</i> -spacing from (ASTM data file) Å	Intensity grading from (ASTM data file)
Product from CuL ₂ at 360°C	1.97	1	Cu _{1.8} S (Digenite)	1.97	1 (100)
	1.69	2		1.68	2 (90)
	2.77	3		2.79	3 (80)
Final Product from CuL ₂	2.50	1	CuO	2.52	1 (100)
	2.30	2		2.32	2 (96)
	1.85	3		1.87	3 (25)
Product from NiL ₂ at 440°C	1.97	1	NiS _{1.03}	1.99	1 (100)
	1.70	2		1.72	2 (80)
	1.30	3		1.30	3 (70)
Final Product from NiL ₂	2.07	1	NiO	2.09	1 (100)
	2.39	2		2.41	2 (91)
	1.47	3		1.48	3 (57)

750° DTG peak corresponds to the 740° endothermic DTA peak and could be attributed to the decomposition of CuSO₄ to CuO. The end product of decomposition was confirmed to be CuO from X-ray pattern (Table 3).

In the case of the nickel complex a somewhat similar pattern is observed. It may be seen from Table 1, that the main decomposition stage is represented

by a DTG peak at 357° corresponding to an exothermic DTA peak at 365°. The loss of mass at the end of the first stage, read from the TG curve, is 70.1%, while the theoretical loss of mass for the decomposition of $\text{NiL}_2 \rightarrow \text{NiS}$ is 74.5%. The agreement here can be considered to be satisfactory, since the discrepancy is attributable to the same reason as for the copper complex. The X-ray powder pattern at this stage showed that NiS is formed (Table 3). The remaining DTA and DTG peaks for NiL_2 are less well-defined and may be attributed to oxidative decomposition processes. The overall loss of mass from the TG curve is 80.6%, whilst the theoretical loss in mass for the conversion $\text{NiL}_2 \rightarrow \text{NiO}$ is 79.0%. The end-product is confirmed to be NiO from its X-ray diffraction pattern (Table 3).

The DTA curves for CuL_2 and NiL_2 each show a very narrow endothermic peak (230° for CuL_2 and 260° for NiL_2) which may be correlated with melting. Independent experiments confirmed this.

In a recent work [6], D'Ascenzo and Wendlandt studied a number of metal diethyl dithiocarbamates by TG and DTA as well as by high temperature reflectance spectroscopy including those of Ni and Cu. In the decomposition ranges reported by these workers are similar to those observed by us. However, their peak temperatures are somewhat lower than ours, because they used smaller masses, higher heating rates and an atmosphere of dynamic air. The influence of these experimental variables on peak temperatures has been discussed by Dharwarkar and Karkhanawala [7]. It may also be noted here that our observations, based on elemental analysis, on the absence of dehydration peaks in DTG and DTA and on the absence of hydroxyl bands in i.r. spectra, indicate that both CuL_2 and NiL_2 are anhydrous, which is in agreement with the observations of Flaherty and McCutcheon [8].

Decomposition kinetics

In studying the decomposition kinetics, it was considered worth-while to try one of each of the differential, integral and approximation methods mentioned in the literature [9]. We chose the Freeman–Carroll, the Coats–Redfern and the Horowitz–Metzger equations. The analysis of data using the Freeman–Carroll equation gives a value of the order of the reaction, $n = 0.90$ for the decomposition of CuL_2 and $n = 1.08$ for that of NiL_2 . However, since the substances melt prior to decomposition, the order may be taken as unity. On this basis, the activation energies are calculated and are found to be 265.5 kJ mole⁻¹ and 263.2 kJ mole⁻¹, for CuL_2 and NiL_2 respectively.

The energy of activation obtained from the application of the Coats–Redfern equation are: for CuL_2 , $E^* = 246.5$ kJ mole⁻¹; for NiL_2 , $E^* = 261.6$ kJ mole⁻¹.

The Horowitz–Metzger equation (for $n = 1$) gives the following values for activation energy $E^* = 264.7$ kJ mole⁻¹ for the decomposition of CuL_2 and $E^* = 282.3$ kJ mole⁻¹ for the decomposition of NiL_2 . The near-unity values of correlation coefficients for the least square plots indicate good agreement between the observed points and the linear least square plots.

From the calculation reported above the activation energies for the decomposition of dithiocarbamate complexes are found to be 250–280 kJ mole⁻¹. These values are comparable to the values generally observed for tetraco-ordinated transition metal complexes reported in literature and are somewhat lower than those for hexaco-ordinated complexes [10].

The entropies of activation are found to be 120–170 J mole⁻¹ K⁻¹. The positive value indicates that the activated complexes are less ordered structures than are to the reactants.

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ZUSAMMENFASSUNG — Die aus thermogravimetrischen (TG), derivativ-thermogravimetrischen (DTG) und differential-thermoanalytischen (DTA) Untersuchungen von CuL₂ und NiL₂ (L⁻ = Diäthyl-dithiocarbamat-Anion) in Luft erhaltenen Kurven wurden diskutiert. Die wichtigsten Temperaturbereiche der Zersetzung sind: für CuL₂ DTG 250–350°C, DTA 300–320°C und für NiL₂ DTG 290–390°C, DTA 360–400°C. Die Gewichtsverluste in den Hauptstufen der Zersetzung deuten auf eine Umwandlung der Komplexe in die Sulfide. Die mathematische Analyse der Ergebnisse zeigt die Anwendbarkeit der Kinetik in beiden Fällen. Die kinetischen Parameter (Aktivierungsenergie und -entropie sowie präexponentieller Faktor) wurden angegeben.

RÉSUMÉ — On a étudié les courbes thermogravimétriques (TG), leurs dérivées (TGD) et les courbes d'analyse thermique différentielle (ATD) dans l'air de CuL₂ et NiL₂ (L⁻ = anion diéthyl-dithiocarbamate). Les principaux intervalles de température où la décomposition s'effectue sont les suivants: pour CuL₂ 250–350° par TGD, 300–320° par ATD et pour NiL₂,

290—390° par TGD, 360—400° par ATD. Les pertes de masse pendant les principales étapes de la décomposition indiquent une conversion des complexes en sulfures. L'analyse mathématique des résultats TG indique qu'une cinétique du premier ordre s'applique dans les deux cas. Les paramètres cinétiques (énergie et entropie d'activation, ainsi que facteur pré-exponentiel) sont communiqués.

Резюме — С помощью термогравиметрического (ТГ), дериватотермогравиметрического (ДТГ) и дифференциального термического анализа (ДТА) были изучены в атмосфере воздуха соединения CuL_2 и NiL_2 , где L^- = диэтилдитиокарбамат анион. По данным ДТГ, главные температурные интервалы распада для CuL_2 и NiL_2 расположены соответственно при 250—350 °С и 290—390 °С. По данным ДТА — соответственно при 300—320 °С и 360—400 °С. Потеря массы при главных стадиях распада указывает на превращение комплексов до сульфидов. Математический анализ данных ТГ показывает, что в обоих случаях применима реакция первого порядка. Приведены такие кинетические параметры как энергия и энтропия активации и предэкспоненциальный фактор.