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KINETIC ANALYSIS OF THERMOGRAVIMETRIC DATA ON SOME NICKEL(II) N-ALKYLDITHIOCARBAMATES

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Thermogravimetric and derivative thermogravimetric curves of some complexes $[Ni(S_2CNHR)_2]$ (R = Me, Et, Pr^i, Bu^i, Bu^t, Bz, *p*-MePh, *p*-MeOPh, *p*-ClPh, *p*-NO_2Ph) in a dynamic nitrogen atmosphere were studied to determine their modes of decomposition. All these complexes show similar TG profiles. The weight losses in the main decomposition stages indicate conversion of the nickel(II) dithiocarbamates to sulphide. Reaction orders were estimated via the shape characteristics of the corresponding derivative thermogravimetric curves and kinetic analysis of the thermogravimetric data was performed by using the Coats–Redfern and Horowitz–Metzger methods.

Dithiocarbamates constitute a class of organo-sulphur compounds with strong binding properties, which are also known to have profound effects on biological systems [1]. Interest in the study of metal dithiocarbamato complexes has been stimulated by their use in industry as vulcanization accelerators and as high-pressure lubricants, whereas their use as fungicides and pesticides has induced a vast number of biological and biochemical investigations [2]. In this respect, several d^8 metal complexes of aliphatic and aromatic dithiocarbamates have already been studied in our laboratory in an attempt to establish the chemical and electronic properties of the various coordination geometries obtainable within the dithio-acid system [3–6]. One logical extension of this work was to study the thermal decomposition of bis(N-monosubstituted-dithiocarbamato)metal(II) complexes, $[M(S_2CNHR)_2]$ (M = Ni, Pd, Pt), as a literature survey revealed that little work has been carried out on thermal studies of metal(II) N-alkyldithiocarbamates [7]. To this end, thermoanalytical data (TG and DTG) on some typical square-planar Ni(II) dithiocarbamates with substituents displaying various electronic effects are reported in the present paper. Moreover, an interpretation and numerical analysis of these data is attempted, since thermogravimetric analysis is an important method for the study of solid-state reactions. However, most of the methods available for the calculation of kinetic parameters, such as the reaction order (*n*), the activation energy (E^*) and the pre-exponential factor (*Z*), from the TG curve are based on trial and error methods [8]. It has also been found that these methods do not reproduce E^* and *n* when the same data set is taken for the computation [9]. In the present paper, the integral method employing the Coats–Redfern equation [10], and the approximation method using the Horowitz–Metzger equation [11], are used for the calculation of kinetic parameters from a nonisothermal kinetic study.

Experimental

Preparation of samples

Samples of bis(N-alkyldithiocarbamato)nickel(II) complexes, $[Ni(S_2CNHR)_2]$ (R = Me, Et, Pr^i, Bu^i, Bu^t, Bz, *p*-MePh, *p*-MeOPh, *p*-ClPh, *p*-No_2Ph), were obtained from the reaction between nickel(II) chloride and the appropriate ammonium dithiocarbamate in dimethylsulphoxide (DMSO) solution [5, 12]. Recrystallization was carried out by dissolving the solid in an acetone-DMSO mixture and reprecipitating with water (yield 85%). The ammonium N-alkyldithiocarbamates were prepared and recrystallized as previously reported [5].

Instruments

The TG and DTG curves were obtained on a DuPont Model 99 Thermal Analyser combined with a DuPont Model 951 Thermogravimetric Analyser. The measurements were performed by using a dynamic nitrogen furnace atmosphere at a flow rate of 60 ml min^{-1} up to 900°. The heating rate was 10 deg per min and the sample sizes ranged in mass from 10 to 12 mg. X-ray powder diffraction analyses of the final residues were made with a Phillips PW 11300/00 X-ray diffractometer, using Cu-K_α radiation ($\lambda = 0.1542$ nm). The elemental analysis of carbon, nitrogen and hydrogen was performed on a Perkin–Elmer 240B microanalyser. Infrared spectra were recorded in the region 4000–250 cm^{-1} on a Perkin–Elmer 467 spectrophotometer, using KBr pellets.

Results and discussion

Thermal analysis

All complexes were studied by thermogravimetric analysis from ambient temperature to 900° in nitrogen atmosphere. The temperature ranges and percentage weight losses of the decomposition reactions are given in Table 1,

Table 1 Thermoanalytical results (TG/DTG) on nickel(II) dithiocarbamates in nitrogen atmosphere

Complex	Stage	Temp. range, °C	DTG$_{max}$, °C	Weight loss, %	Evolved moiety	Weight loss calc., %
[Ni(S_2CNHMe)$_2$]	1	170–250	210	65.6	S_2CNHMe +SCNHMe	66.40
	2	600–850	—	12.1	S	11.81
	residue	>850	—	22.0	Ni°	21.77
[Ni(S_2CNHEt)$_2$]	1	140–250	182	69.6	S_2CNHEt +SCNHEt	69.56
	2	250–600	—	11.5	S	10.70
	residue	>850	—	19.0	Ni°	19.73
[Ni(S_2CNHPr^i)$_2$]	1	150–225	200	70.0	S_2CNHPr^i +SCNHPr^i	76.55
	2	225–600	—	18.0	S+unknown	9.78+?
	residue	>850	—	12.0	Ni°	18.04
[Ni(S_2CNHBu^i)$_2$]	1	160–225	202	74.8	S_2CNHBu^i +SCNHBu^i	74.43
	2	450–700	—	9.3	S	9.02
	residue	>850	—	16.3	Ni°	16.55
[Ni(S_2CNHBu^t)$_2$]	1a	120–195	175	59.4	S_2CNHBu^t+NHBu^t	62.0
	1b	195–225	205	14.0	SC	12.43
	2	400–700	—	9.3	S	9.02
	residue	>850	—	16.4	Ni°	16.55
[Ni(S_2CNHBz)$_2$]	1a	175–215	225	41.0	S_2CNHBz	43.02
	1b	215–250	230	37.0	SCNHBz	35.46
	intermediate	250–450	—	22.0	NiS	21.52
[Ni(S_2CNH-*p*-MePh)$_2$]	1	155–220	200	77.5	S_2CNH*p*-MePh +SCNH*p*-MePh	78.48
	2	600–850	—	6.5	S	7.56
	residue	>850	—	16.0	Ni°	13.95

Table 1 (continued)

Complex	Stage	Temp. range, °C	DTG_{max}, °C	Weight loss, %	Evolved moiety	Weight loss calc., %
$[Ni(S_2CNH$*p*-$MeOPh)_2]$	1	160–225	200	79.0	S_2CNH*p*-MeOPh +SCNH*p*-MeOPh	80.00
	2	550–850	—	5.5	S	7.04
	residue	>850	—	15.5	Ni°	12.96
$[Ni(S_2CNH$*p*-$ClPh)_2]$	1	100–250	200	78.0	S_2CNH*p*-ClPh +SCNH*p*-ClPh	80.39
	2	600–850	—	8.5	S	6.89
	residue	>850	—	13.5	Ni°	12.71
$[Ni(S_2CNH$*p*-$NO_2Ph)_2]$	1	135–250	212	81.0	S_2CNH*p*-NO_2Ph +SCNH*p*-NO_2Ph	81.24
	2	400–850	—	7.0	S	6.59
	residue	>850	—	12.0	Ni°	12.16

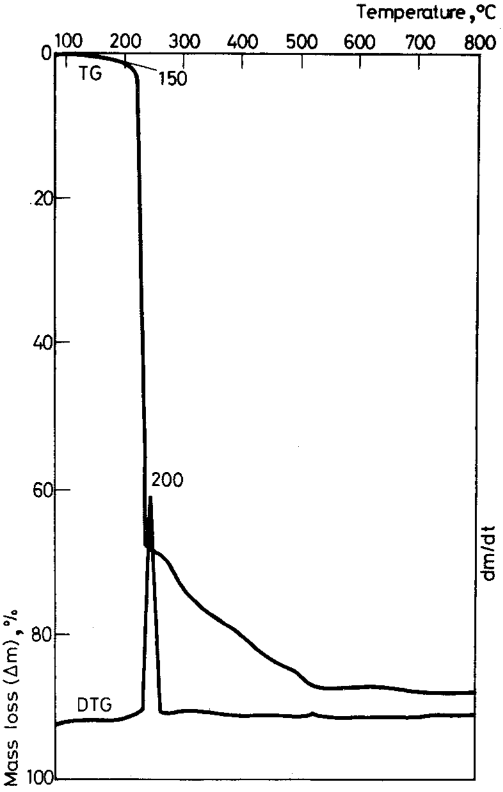

Fig. 1 Thermoanalytical curves of $[Ni(S_2CNHPr^i)_2]$ in nitrogen

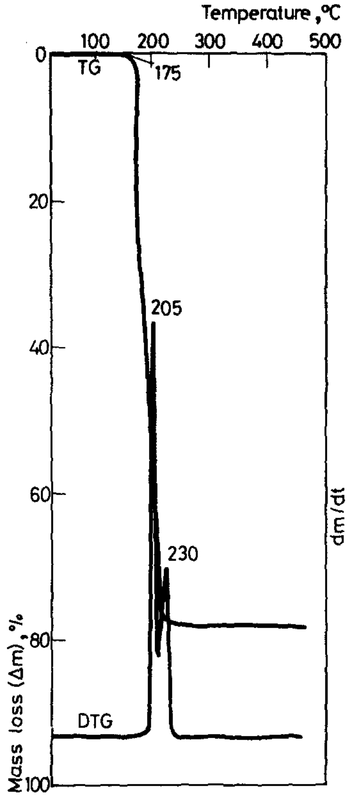

Fig. 2 Thermoanalytical curves of $[Ni(S_2CNHBz)_2]$ in nitrogen

together with the temperatures of greatest rate of decomposition (DTG_{max}) and the theoretical percentage weight losses. The thermal curves obtained for most of the compounds were very similar in character. All complexes show two-stage weight loss in their TG/DTG curves in a nitrogen atmosphere. The first weight loss corresponds to the formation of their respective sulphides, while the second weight loss is due to the decomposition of the sulphides. The intermediates and end-products were confirmed via the elemental analyses and X-ray diffraction data. It may also be noted here that the results of elemental analysis, the absence of dehydration peaks in the DTG curves and the absence of hydroxy bands in the IR spectra indicate that all the compounds under investigation are anhydrous, which is in agreement with our previous studies [5, 12]. The TG and DTG curves of $[Ni(S_2CNHPr^i)_2]$, $[Ni(S_2CNHBz)_2]$ and $[Ni(S_2CNHpMePh)_2]$ are presented in Figs 1–3.

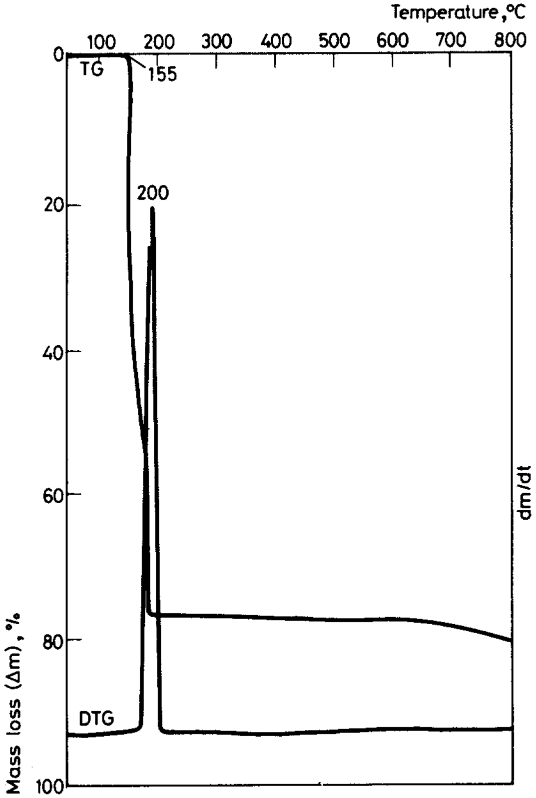

Fig. 3 Thermoanalytical curves of $[Ni(S_2CNH\textit{p}\text{-}MePh)_2]$ in nitrogen

In general, decomposition begins between 100 and 170°, followed by a rapid weight loss of over 60%. It was presumed that metal sulphide is formed at the end of this step, the calculated weight losses showing close agreement with the experimental values. The residue at this stage was also analysed for sulphur content. Consequently, the weight loss at this stage is attributed to the evolved moieties $\{S_2CNHR + SCNHR\}$, according to the following reaction:

$$[Ni(S_2CNHR)_2] \rightarrow NiS + \{RHNC(S)S + RHNCS\}$$

In the cases of $[Ni(S_2CNHBu^t)_2]$ and $[Ni(S_2CNHBz)_2]$, however, the decomposition of nickel(II) dithiocarbamate to metal sulphide is observed to occur in two substeps (see Table 1) the first weight loss corresponds to the elimination of one dithiocarbamato group, followed by the elimination of one thiocarbamoylo group and the formation of metal sulphide after the second weight loss. This main decomposition step is followed by a final weight loss at around 600°, leaving a stable residue of nickel at 850°.

Decomposition kinetics

The decomposition curves for $[Ni(S_2CNHR)_2]$ in general exhibit a characteristic, well-defined and non-overlapping decomposition pattern. The first stage is the major decomposition step in each case, the weight losses, elemental analyses and X-ray powder patterns indicating the product to be NiS. The first stage was chosen for a detailed study. The reaction orders (n) were determined from the shape characteristics of the corresponding DTG curves by using the following approximation [13–16]:

$$X_M \approx 1 - n^{1/(1-n)} \tag{1}$$

where X_M is the conversion at the maximum decomposition rate. Kinetic parameters were next evaluated graphically by employing the Coats–Redfern equation [10]:

$$\log \frac{\left[1 - \left(\frac{W_\alpha - W}{W_\alpha}\right)^{1-n}\right]}{(1-n)T^2} = \log \frac{ZR}{\Phi E^*}\left[1 - \frac{2RT}{E^*}\right] - \frac{E^*}{2.3R}\frac{1}{T} \tag{2}$$

where w_α = total mass loss in the first stage and Φ = rate of heating (deg min^{-1}). Since $1 - 2RT/E^* \approx 1$, the left-hand side expression was plotted against $1/T$ (Figs 4 and 5), from the slope of which E^* was calculated. This value of E^* was used to calculate Z from the intercept. Finally, the entropies of activation (ΔS^*) were

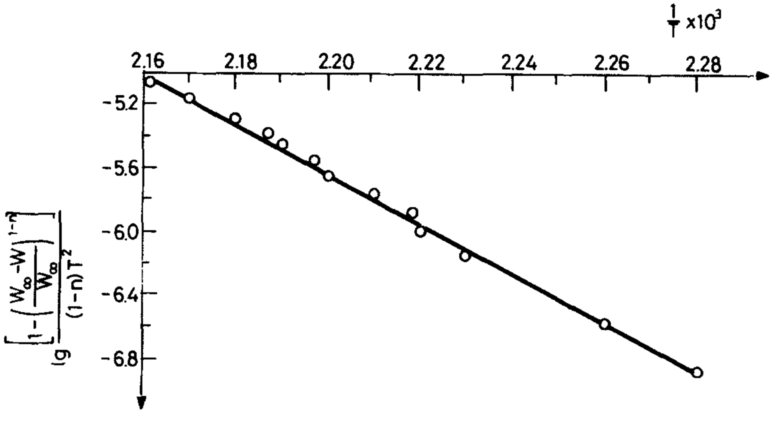

Fig. 4 Coats–Redfern plot for $[Ni(S_2CNHBu^i)_2]$

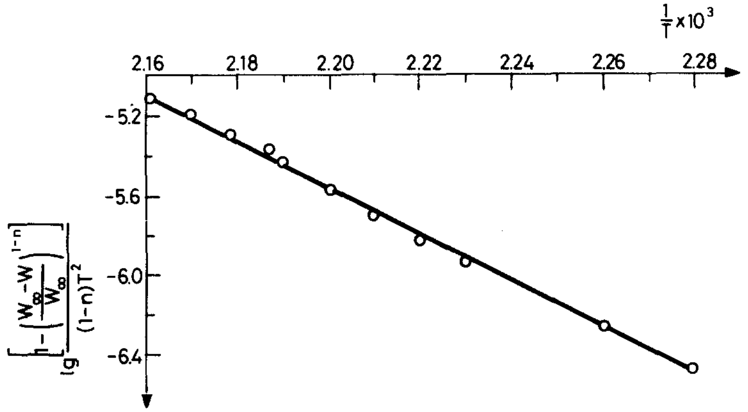

Fig. 5 Coats–Redfern plot for [Ni(S_2CNH*p*-ClPh)$_2$]

obtained from the equation [17]:

$$Z=\frac{kT_i}{h}\exp\left(\frac{\Delta S^*}{R}\right) \tag{3}$$

where k is the Boltzmann constant, h is Planck's constant and T_i is the temperature at the DTG peak.

The kinetic parameters obtained by this procedure are listed in Table 2. The reaction orders and the correlation coefficients (r) of the corresponding linear plots are also given.

As shown in Table 2, the near-unity values of the correlation coefficients for the least square refinements indicate good agreement. Moreover, the activation energies for the decomposition of nickel(II) N-alkyldithiocarbamates were found to be comparable with the values previously reported for the square-planar d^8 metal(II) dithio complexes [7, 18]. These values are also comparable with the values generally observed for four-coordinated transition metal complexes [19]. Finally, the positive values of entropies of activation indicate that the activated complexes have less ordered structures than the reactants.

In dynamic rate equations, the activation energy and order of reaction are not proportionally dependent on each other. Hence, for a given value of n, the different relations need not necessarily yield the same E^* value [9]. It is therefore advisable to use more than one method to treat the data when trying to ascertain the correct activation energy. For this reason, it was considered worthwhile to try one more method mentioned in the literature [15, 17], and for this the Horowitz–Metzger equation [11] was chosen:

$$\log\left[1-\left(\frac{w_\alpha-w}{w_\alpha}\right)^{1-n}\right]=\log(1-n)+\frac{E^*}{2.3RT_i^2}\theta \tag{4}$$

Table 2 Kinetic data on the investigated compounds, obtained with the Coats–Redfern equation

Complex	Parameters†			
	E^*, kJ mol^{-1}	Z, s^{-1}	ΔS^*, J mol^{-1} K^{-1}	r
[Ni(S_2CNHMe)$_2$] $w_\alpha = 4.53$ mg $n = 0.877$	287.4	3.39×10^{30}	482.3	0.986
[Ni(S_2CNHEt)$_2$] $w_\alpha = 10.09$ mg $n = 0.811$	262.3	3.38×10^{29}	463.4	0.990
[Ni(S_2CNHPr^i)$_2$] $w_\alpha = 5.36$ mg $n = 0.723$	297.5	1.89×10^{32}	515.8	0.985
[Ni(S_2CNHBu^i)$_2$] $w_\alpha = 4.76$ mg $n = 0.506$	293.7	6.99×10^{31}	507.4	0.994
[Ni(S_2CNHBu^t)$_2$] $w_\alpha = 5.28$ mg $n = 0.589$	227.9	3.31×10^{24}	367.0	0.980
[Ni(S_2CNHBz)$_2$] $w_\alpha = 4.53$ mg $n = 0.420$	107.3	4.12×10^{9}	81.3	0.986
[Ni(S_2CNHp-MePh)$_2$] $w_\alpha = 10.09$ mg $n = 0.443$	158.0	2.07×10^{16}	209.9	0.992
[Ni(S_2CNHp-MeOPh)$_2$] $w_\alpha = 5.36$ mg $n = 0.437$	229.6	3.55×10^{24}	367.5	0.978
[Ni(S_2CNHp-ClPh)$_2$] $w_\alpha = 4.76$ mg $n = 0.468$	222.9	4.72×10^{23}	350.7	0.996
[Ni(S_2CNHp-NO_2Ph)$_2$] $w_\alpha = 5.28$ mg $n = 0.480$	186.5	6.40×10^{18}	257.3	0.992

†w_α = total mass loss for the particular decomposition stage; r = correlation coefficient of the linear plot.

where θ is the difference between the given temperature T and the temperature T_i corresponding to the maximal decomposition rate.

A plot of the left-hand side expression *vs.* θ was found to be linear, from the slope of which E^* was calculated. Typical curves relating to the application of the above equation are given in Figs 6 and 7. All the linear plots were drawn by the method of least squares and the corresponding correlation coefficients (r) were also calculated. The pre-exponential factor Z was calculated from the equation [15]:

$$\frac{E^*}{RT_i^2} = \frac{Z}{\Phi} \mathrm{n} c_i^{n-1} \exp\left(-\frac{E^*}{RT_i}\right) \tag{5}$$

The entropy of activation ΔS^* was calculated from Eq. (3). Kinetic parameters calculated by employing the above equations are given in Table 3.

The results reveal that the activation energy calculated for $[Ni(S_2CNHEt)_2]$ with the Coats and Redfern method, 262.3 kJ mol^{-1}, is in good agreement with the

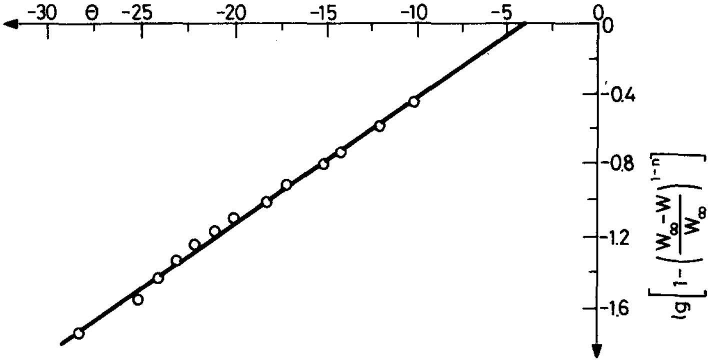

Fig. 6 Horowitz–Metzger plot for $[Ni(S_2CNHMe)_2]$

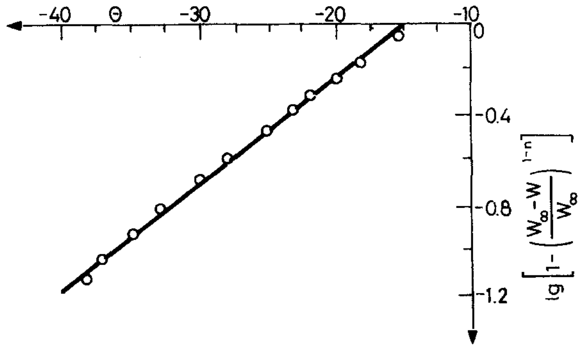

Fig. 7 Horowitz–Metzger plot for $[Ni(S_2CNH\textit{p}\text{-}MePh)_2]$

Table 3 Kinetic data on the investigated compounds, obtained with the Horowitz–Metzger equation

Complex	Parameters*			
	E^*, kJ mol^{-1}	Z, s^{-1}	ΔS^*, J mole^{-1} K^{-1}	r
$[Ni(S_2CNHMe)_2]$	317.6	5.43×10^{32}	524.2	0.996
$[Ni(S_2CNHEt)_2]$	293.7	1.35×10^{32}	513.3	0.964
$[Ni(S_2CNHPr^i)_2]$	261.9	1.69×10^{27}	419.0	0.987
$[Ni(S_2CNHBu^i)_2]$	333.1	1.13×10^{35}	569.0	0.994
$[Ni(S_2CNHBu^t)_2]$	232.1	4.44×10^{23}	350.3	0.988
$[Ni(S_2CNHBz)_2]$	109.4	8.59×10^{9}	87.6	0.992
$[Ni(S_2CNH$*p*-$MePh)_2]$	197.3	1.02×10^{20}	280.7	0.997
$[Ni(S_2CNH$*p*-$MeOPh)_2]$	313.0	9.61×10^{32}	529.2	0.986
$[Ni(S_2CNH$*p*-$ClPh)_2]$	257.3	5.59×10^{26}	409.8	0.993
$[Ni(S_2CNH$*p*-$NO_2Ph)_2]$	230.0	1.07×10^{23}	338.1	0.995

* r = correlation coefficient of the linear plot.

reported value of 261.6 kJ mol^{-1} [17] for the decomposition of $[Ni(S_2CNEt_2)_2]$. If we assume that the activation energy calculated with the Coats and Redfern method is nearly correct, then the activation energy calculated with the Horowitz and Metzger method has a 12% error. Nevertheless, we should not discard the latter method, as it may give better results in other examples [9].

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Zusammenfassung — Im Stickstoffstrom wurden TG- und DTG-Kurven einiger Komplexe $[Ni(S_2CNHR)_2]$ mit R = Me, Et, Pr^i, Bu^i, Bu^t, Bz, *p*-MePh, *p*-MeOPh, *p*-ClPh und *p*-NO_2Ph ermittelt, um Art und Weise ihrer Zersetzung zu bestimmen. Alle diese Komplexe zeigen ähnliche TG-Profile. Die Gewichtsverluste der Hauptzersetzungsschritte weisen auf eine Umwandlung der Nickel(II)dithiokarbamate in Sulfide hin. Aus dem Verlauf der korrespondierenden DTG-Kurven wurde auf die Reaktionsordnung geschlossen und unter Anwendung der Coats–Redfern und Horowitz–Metzger Methoden wurde eine kinetische Analyse der TG-Daten durchgeführt.

Резюме — С целью определения характера разложения комплексов $[Ni(S_2CNHR)_2]$, где R = Me, Et, *i*-Pr, *i*-Bu, *t*-Bu, Bz, *p*-MePh, *p*-MeOPh, *p*-ClPh и *p*-NO_2Ph, были измерены в динамической атмосфере азота кривые ТГ и ДТГ. Все комплексы показали подобный характер ТГ кривых. Потери веса на главных стадиях разложения указывают на превращение дитиокарбаматов никеля до его сульфида. Порядок реакций был определен посредством модельных характеристик соответствующих ДТГ кривых и кинетического анализа данных ТГ, проведенного методами Коутса–Рэдферна и Хоровиц–Мецгера.