

Carbodithioato derivatives of weak nitrogenous nucleophiles.

Part 4. Mass spectra and thermal decomposition kinetics of Ni(II) *N*-carbodithioates with substituted ureas, carbamic esters and sulfonamides

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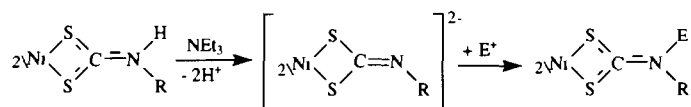
Abstract

Mass spectral and thermal studies by TG/DTG analysis of Ni[S₂CN(E)R]₂ complexes (where E is CONHPh, CONPh₂, COOEt or ArSO₂, and R is Me, Buⁿ or Bz) in dynamic nitrogen atmosphere have been carried out to determine their modes of decomposition. In this respect, fragmentation patterns are given and possible mechanisms are discussed. Reaction orders were estimated employing the Freeman–Carroll equation. A kinetic analysis of the thermogravimetric data was performed using the Coats–Redfern equation to determine the apparent activation energies and the pre-exponential factor of the Arrhenius equation.

INTRODUCTION

We recently reported [1–4] that treatment of the square-planar nickel(II) *N*-alkyldithiocarbamates, Ni(S₂CNHR)₂, with a wide diversity of electrophiles (E⁺), such as secondary amides, ureas, carbamic esters and sulfonamides, in the presence of triethylamine as a deprotonating agent, results in the formation of nickel(II) carbodithioates of the general formula Ni[S₂CN(E)R]₂. This electrophilic substitution reaction proceeds via a unimolecular (S_E1) mechanism [1], involving the formation of [Ni(S₂C=NR)₂]²⁻ complexes as a transition state [5], according to Scheme 1.

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Scheme 1.

The thermal decomposition [6] of the acylation products of the aforesaid reaction, namely the nickel(II) amide *N*-carbodithioates, $\text{Ni}[\text{S}_2\text{CN}(\text{COR}')\text{R}]_2$, showed a one-stage weight loss corresponding to the formation of nickel sulphide. From a non-isothermal kinetic study of this decomposition reaction, the activation energy was found to be approx. 155 kJ mol^{-1} . This value is significantly lower than the reported one [7–9] of approx. 262 kJ mol^{-1} for the decomposition of $\text{Ni}(\text{S}_2\text{CNHR})_2$, a fact which may be attributed to the strong electron-withdrawing ability of the acetyl group of the former complexes. Therefore, the logical extension of this work is to study the thermal behaviour of other classes of carbodithioato complexes in an attempt to assess the effect of electrophilic substitution in the S_2CNHR system on the strength of metal–sulphur bonds. To this end, thermoanalytical data (TG and DTG) of several $\text{Ni}[\text{S}_2\text{CN}(\text{E})\text{R}]_2$ complexes (E is CONHPh , CONPh_2 , CO_2Et or ArSO_2 ; R is Me, Bu^n or Bz) are reported in the present paper. In addition, the interpretation and numerical analysis of thermoanalytical data are given, as well as the evaluation of the order of reaction, the energy of activation and the pre-exponential factor, based on the differential method of Freeman and Carroll [10], and the integral method of Coats and Redfern [11].

EXPERIMENTAL

Preparation of samples

Samples of $\text{Ni}[\text{S}_2\text{CN}(\text{E})\text{R}]_2$ complexes were obtained [3] from the reaction of acetone solutions of the appropriate bis(*N*-alkyldithiocarbamato) nickel(II) complex with the appropriate precursor of the corresponding electrophile, e.g. Ph_2NCOCl , ClCOOEt , PhSO_2Cl or *p*- MePhSO_2Cl , in the presence of triethylamine (1:2:2 molar ratios). The complexes were recrystallized from acetone solutions (yield: approx. 75%).

Instruments

Mass spectra were measured on a RMU-6L Hitachi Perkin-Elmer mass spectrometer with an ionization source of T-2p type operating at 70 eV. The

TG/DTG curves were obtained on a Perkin-Elmer 7 Series Thermal Analysis System. The measurements were performed using a dynamic nitrogen furnace atmosphere at a flow rate of 60 ml min⁻¹ up to 900°C. The heating rate was 20°C min⁻¹ and the sample sizes ranged in mass from 8 to 13 mg. The elemental analysis of carbon, nitrogen and hydrogen was performed on a Perkin-Elmer 240B microanalyser.

RESULTS AND DISCUSSION

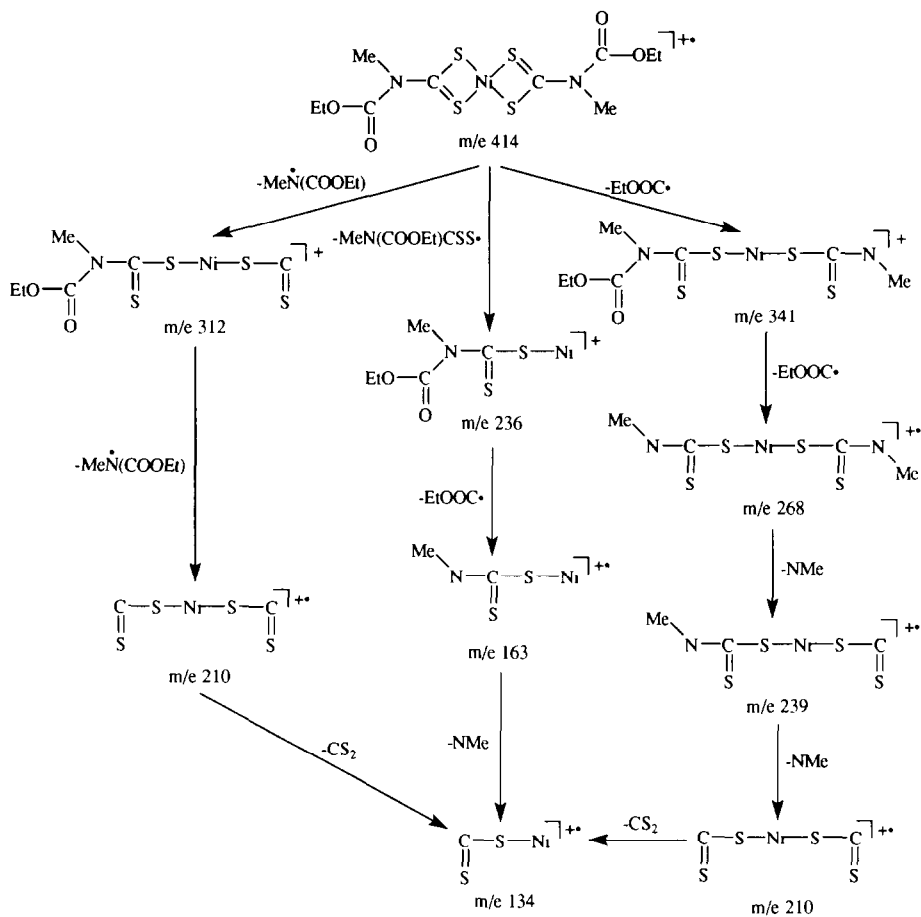
Mass spectral studies

The molecular ions of the studied compounds could not be detected in the mass spectra, except in the case of Ni[S₂CN(COOEt)R]₂ complexes. The absence of molecular ions can be attributed to decomposition, either pyrolytically in the direct inlet under the high temperature which was used (200–280°C), or to electron impact. The main mass spectral peaks of the compounds studied are given in Table 1, and a simplified picture of the

TABLE 1

Main mass spectral peaks of nickel(II) *N*-carbodithioates

Compound	<i>m/z</i> (relative intensity)
Ni[S ₂ CN(PhHNCO)Me] ₂	76(13), 77(100), 98(99), 105(66), 121(14), 134(17), 149(12), 165(12), 213(8), 225(13), 239(20), 257(13), 261(20), 268(11), 275(8), 284(12), 335(23), 360(12), 389(15)
Ni[S ₂ CN(Ph ₂ NCO)Me] ₂	76(20), 77(31), 117(18), 174(55), 200(51), 202(67), 207(15), 227(12), 240(14), 242(43), 244(60), 268(22), 277(19), 283(44), 285(21), 301(9), 360(11), 465(8)
Ni[S ₂ CN(COOEt)Me] ₂	76(42), 77(74), 103(100), 134(55), 162(20), 179(42), 193(51), 197(64), 210(11), 236(21), 239(51), 268(13), 312(12), 345(15), 382(11), 411(16), 414(18)
Ni[S ₂ CN(COOEt)Bu ⁿ] ₂	77(100), 115(71), 134(29), 144(37), 163(31), 192(16), 210(22), 219(13), 235(22), 262(16), 278(11), 281(27), 295(8), 352(11), 355(27), 425(9), 435(10), 472(14), 498(18)
Ni[S ₂ CN(COOEt)Bz] ₂	58(100), 76(58), 105(11), 134(12), 149(36), 178(32), 210(27), 240(19), 254(22), 281(8), 310(32), 313(21), 359(38), 381(74), 389(37), 420(19), 438(12), 493(9), 566(8)
Ni[S ₂ CN(PhSO ₂)Me] ₂	28(100), 77(28), 110(58), 134(27), 139(50), 163(31), 210(76), 239(17), 246(21), 251(36), 268(29), 281(16), 305(24), 312(25), 354(74), 374(9), 381(13), 410(11), 503(18)
Ni[S ₂ CN(<i>p</i> -MePhSO ₂)Me] ₂	62(100), 76(36), 91(46), 134(28), 155(46), 163(31), 184(28), 200(11), 210(27), 239(10), 252(18), 260(32), 268(21), 319(14), 395(18), 424(11), 512(12)
Ni[S ₂ CN(<i>p</i> -MePhSO ₂)Bu ⁿ] ₂	71(76), 76(82), 91(100), 155(94), 206(35), 210(76), 226(18), 282(16), 302(15), 353(8), 361(28), 382(22), 436(21), 467(9), 508(8)
Ni[S ₂ CN(<i>p</i> -MePhSO ₂)Bz] ₂	76(72), 89(23), 92(40), 106(100), 119(12), 123(24), 134(32), 155(31), 210(7), 240(9), 260(13), 336(8), 395(16), 421(14), 471(11), 576(5)



Scheme 2. Possible fragmentation pattern of $\text{Ni}[\text{S}_2\text{CN}(\text{COOEt})\text{Me}]_2$ complex.

main fragmentation pathways for $\text{Ni}[\text{S}_2\text{CN}(\text{COOEt})\text{Me}]_2$ is presented in Scheme 2.

The mass spectra of the studied compounds are very similar in character to those obtained for the $\text{Ni}[\text{S}_2\text{CN}(\text{COR}')\text{R}]_2$ complexes [6]. Thus, in all spectra, the ion $[\text{Ni}(\text{SC}(\text{:S})\text{NR})_2]^{++}$ is present (: represents a double bond), and can be regarded as a direct fragment of the molecular ion formed upon elimination of the corresponding electrophilic groups. This is further supported by the detection of a peak with varying relative intensity (70–100%) because of the $[\text{E}]^+$ ion. The highest mass number ions observed for all compounds, which might be direct fragments of the molecular ion, are those of the formulae $[\text{NiSC}(\text{:S})\text{N}(\text{E})\text{R}]^+$ and $[(\text{SCS})\text{NiSC}(\text{:S})\text{N}(\text{E})\text{R}]^+$. The former ion is probably due to the cleavage of one Ni–S bond and the loss of a carbodithioate radical. A number of daughter ions besides the ones mentioned above were also detected. All these ions showed the characteristic mass distribution expected for the

TABLE 2
Thermoanalytical results for nickel(II) *N*-carbodithioates in nitrogen atmosphere

Compound	Step	Temperature range/(°C)	Weight loss in %	Assignment	Calc. weight loss in %
Ni[S ₂ CN(PhHNCO)Me] ₂	1	151–207	44.1	S ₂ CN(PhHNCO)Me	44.24
	2a	207–228	29.3	N(Me)CONHPh	29.29
	2b	228–250	8.4	SC	8.65
	Residue	>250	18.2	NiS	17.82
Ni[S ₂ CN(Ph ₂ NCO)Me] ₂	1	88–209	44.7	S ₂ CN(Ph ₂ NCO)Me	45.56
	2	209–418	40.6	SCN(Ph ₂ NCO)Me	40.71
Ni[S ₂ CN(COOEt)Me] ₂	Residue	>418	14.7	NiS	13.73
	1	150–300	77.3	S ₂ CN(COOEt)Me + SCN(COOEt)Me	78.14
	Residue	>300	22.7	NiS	21.86
Ni[S ₂ CN(COOEt)Bu ⁿ] ₂	1	150–300	81.0	S ₂ CN(COOEt)Bu ⁿ + SCN(COOEt)Bu ⁿ	81.81
	Residue	>300	19.0	NiS	18.19
Ni[S ₂ CN(COOEt)Bz] ₂	1a	125–262	75.3	S ₂ CN(COOEt)Bz + N(COOEt)Bz	76.23
	1b	262–340	7.4	SC	7.77
	Residue	>340	17.3	NiS	16.00
Ni[S ₂ CN(PhSO ₂)Me] ₂	1	103–260	37.7	SCN(PhSO ₂)Me	38.86
	2	260–425	39.4	SCN(PhSO ₂)Me	38.86
Ni[S ₂ CN(<i>p</i> -MePhSO ₂)Me] ₂	Residue	>425	22.9	NiS + S	22.28
	1	161–259	43.6	S ₂ CN(<i>p</i> -MePhSO ₂)Me	44.93
	2	259–400	32.5	CN(<i>p</i> -MePhSO ₂)Me	33.86
Ni[S ₂ CN(<i>p</i> -MePhSO ₂)Bu ⁿ] ₂	Residue	>400	23.9	NiS + S	21.20
	1	134–253	41.6	SCN(<i>p</i> -MePhSO ₂)Bu ⁿ	40.74
	2	253–403	39.6	SCN(<i>p</i> -MePhSO ₂)Bu ⁿ	40.74
	Residue	>403	18.8	NiS + S	18.52
Ni[S ₂ CN(<i>p</i> -MePhSO ₂)Bz] ₂	1	132–267	41.9	SCN(<i>p</i> -MePhSO ₂)Bz	41.61
	2	267–400	42.2	SCN(<i>p</i> -MePhSO ₂)Bz	41.61
	Residue	>400	15.9	NiS + S	16.79

isotopic composition of nickel. Furthermore, we might expect low relative abundances of these ions, considering the known thermal instability of similar compounds and organometallic compounds in general [12]. Among the most interesting and prominent peaks detected in the high mass region of the spectra of all the examined compounds are those corresponding to the ions $[\text{RN}(\text{E})\text{C}(\text{:S})\text{S}]^{+}$ and $[\text{RN}(\text{E})\text{CS}]^{+}$. These ions may be partly considered as pyrolytic products because their relative intensities are affected by the temperature and the time spent in the direct inlet. Finally, in the lower mass region of the spectra, a number of the detected peaks can be satisfactorily accounted for by the fragment ion $[\text{RN}(\text{E})\text{C}(\text{:S})\text{S}]^{+}$.

Thermal behaviour

All complexes were studied by thermogravimetric analysis from room temperature to 900°C in nitrogen atmosphere. The temperature ranges and percentage weight losses of the decomposition reactions are given in Table 2. The thermograms obtained for the various classes of carbodithioates are very different in character, clearly demonstrating the dependence of thermal decomposition on the electronic effects induced by several substituents within the dithio-acid system. Typical thermoanalytical curves are depicted in Figs. 1–3.

The proposed stages of the thermal degradation of nickel(II) *N*-

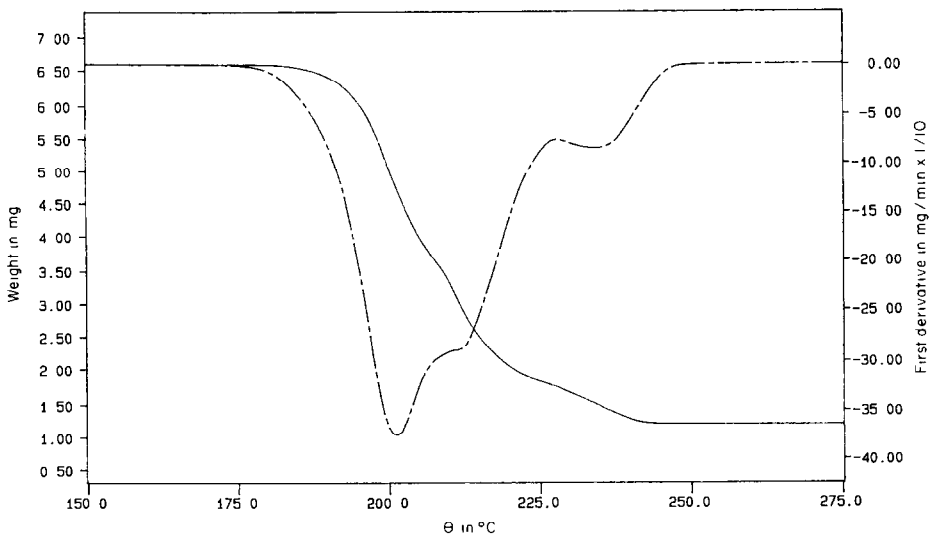


Fig. 1. Thermoanalytical curves of $\text{Ni}[\text{S}_2\text{CN}(\text{PhHNCO})\text{Me}]_2$ in nitrogen.

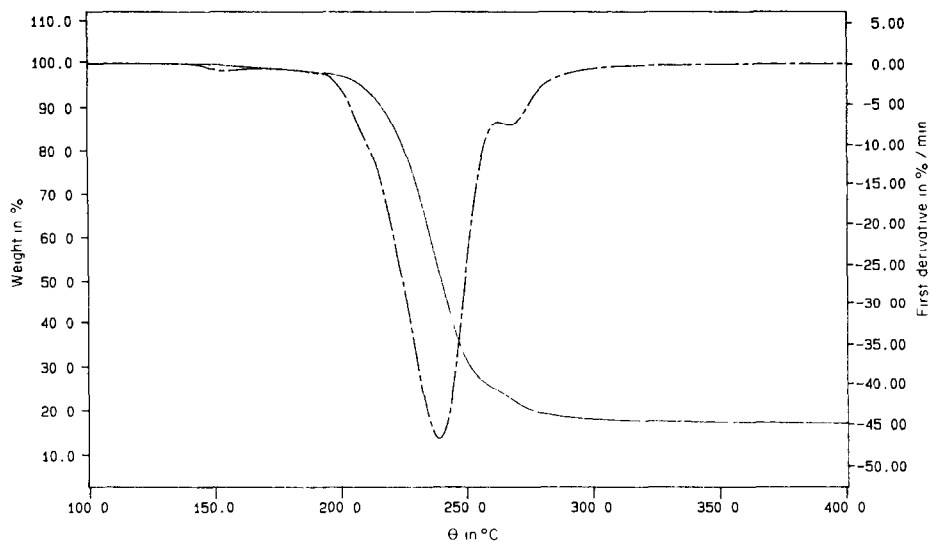
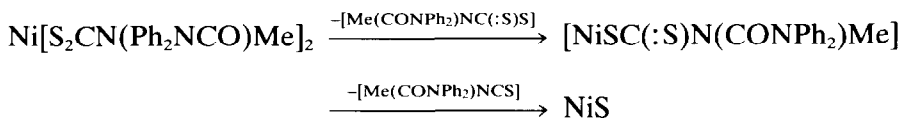


Fig. 2. Thermoanalytical curves of $\text{Ni}[\text{S}_2\text{CN}(\text{COOEt})\text{Bz}]_2$ in nitrogen.

carbodithioates with substituted ureas are



The theoretical weight losses are consistent with the observed ones in each

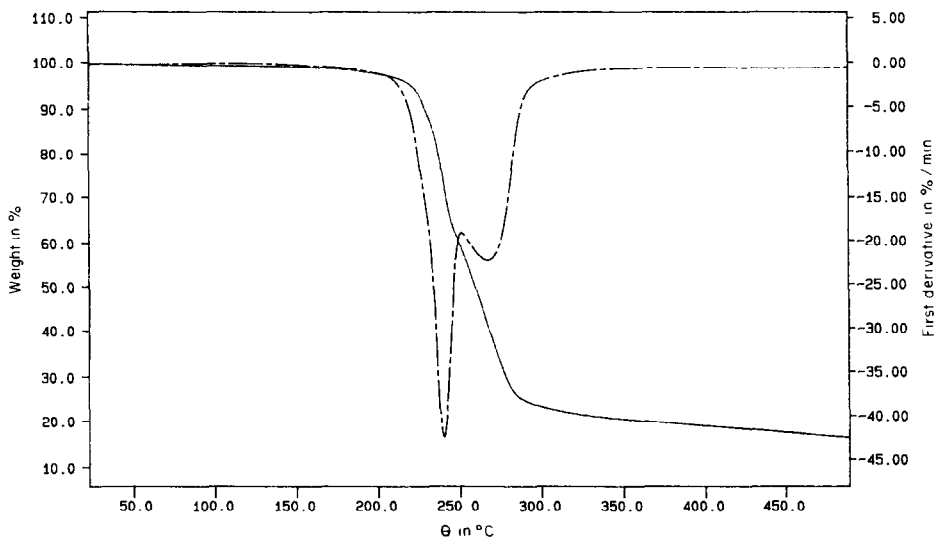


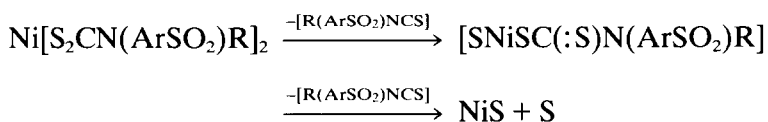
Fig. 3. Thermoanalytical curves of $\text{Ni}[\text{S}_2\text{CN}(p\text{-MePhSO}_2)\text{Bu}^n]_2$ in nitrogen.

particular transition stage; the intermediate is unstable and undergoes further rapid decomposition. This is a two-stage reaction which leads to nickel sulphide through a consecutive cleavage of the Ni–S and C–S bonds and the elimination of one dithiocarbamate and one thiocarbamoyl group, respectively. Thus, the main event in either electron-impact fragmentation or thermal degradation seems to be the elimination of an $[\text{RN}(\text{E})\text{C}(\text{:S})\text{S}]$ group.

In contrast, the complexes with carbamic esters show a thermal behaviour similar to that observed for the corresponding derivatives with secondary amides [6]. In general, decomposition begins between 125 and 150°C, followed by a rapid weight loss of over 75%. It is presumed that nickel sulphide is formed as a stable residue, the calculated weight loss showing close agreement with the experimental values. Consequently, the weight loss is attributed to the evolved moieties $[\text{S}_2\text{CN}(\text{COOEt})\text{R} + \text{SCN}(\text{COOEt})\text{R}]$, according to



Finally, the $\text{Ni}[\text{S}_2\text{CN}(\text{ArSO}_2)\text{R}]_2$ complexes decompose in two nearly overlapping stages



The first weight loss corresponds to the elimination of one thiocarbamoyl group, followed by the elimination of a second one, and the formation of metal sulphide and elemental sulphur after the second weight loss. This residue was also analysed for its sulphur content. The proposed model of decomposition is speculative, because there is no possibility of isolating an intermediate between the first and second stages of degradation. Evidence for a two-stage reaction arises strictly from the TG and DTG curves.

Decomposition kinetics

For the first stage of the decomposition, involving elimination of either a dithiocarbamate or a thiocarbamoyl group, the activation energy E^* and pre-exponential factor Z were calculated.

The activation energy of thermal decomposition can be explained in terms of the probability that a molecule will possess energy in excess of an amount E^* per mole at temperature T , and it is related to the Boltzmann factor $e^{-E^*/RT}$, where R is the molar gas constant. The reaction rate will clearly be dependent on the product of Z and $e^{-E^*/RT}$, where Z is the frequency factor representing the total frequency encounters between two reactant molecules, irrespective of whether they possess sufficient energy or

TABLE 3
Kinetic data for nickel(II) *N*-carbodithioates

Compound	Parameter	Value	
		Freeman–Carroll equation	Coats–Redfern equation
Ni[S ₂ CN(PhHNCO)Me] ₂	<i>E</i> * (kJ mol ⁻¹)	170.4	194.6
	<i>Z</i> (s ⁻¹)	3.79 × 10 ¹⁷	9.81 × 10 ¹⁹
	<i>r</i>	0.986	0.993
Ni[S ₂ CN(Ph ₂ NCO)Me] ₂	<i>E</i> * (kJ mol ⁻¹)	87.4	94.2
	<i>Z</i> (s ⁻¹)	1.02 × 10 ⁸	5.50 × 10 ⁸
	<i>r</i>	0.982	0.989
Ni[S ₂ CN(COOEt)Me] ₂	<i>E</i> * (kJ mol ⁻¹)	139.2	191.3
	<i>Z</i> (s ⁻¹)	3.72 × 10 ¹²	1.03 × 10 ¹⁸
	<i>r</i>	0.981	0.996
Ni[S ₂ CN(COOEt)Bu ⁿ] ₂	<i>E</i> * (kJ mol ⁻¹)	126.1	144.2
	<i>Z</i> (s ⁻¹)	1.08 × 10 ¹¹	8.17 × 10 ¹²
	<i>r</i>	0.948	0.998
Ni[S ₂ CN(COOEt)Bz] ₂	<i>E</i> * (kJ mol ⁻¹)	75.8	98.5
	<i>Z</i> (s ⁻¹)	3.43 × 10 ⁵	8.67 × 10 ⁷
	<i>r</i>	0.958	0.989
Ni[S ₂ CN(PhSO ₂)Me] ₂	<i>E</i> * (kJ mol ⁻¹)	120.3	116.8
	<i>Z</i> (s ⁻¹)	2.13 × 10 ¹⁰	9.14 × 10 ⁹
	<i>r</i>	0.979	0.991
Ni[S ₂ CN(<i>p</i> -MePhSO ₂)Me] ₂	<i>E</i> * (kJ mol ⁻¹)	99.2	109.8
	<i>Z</i> (s ⁻¹)	1.88 × 10 ⁸	2.29 × 10 ⁹
	<i>r</i>	0.988	0.991
Ni[S ₂ CN(<i>p</i> -MePhSO ₂)Bu ⁿ] ₂	<i>E</i> * (kJ mol ⁻¹)	113.2	116.4
	<i>Z</i> (s ⁻¹)	5.83 × 10 ⁹	1.08 × 10 ¹⁰
	<i>r</i>	0.981	0.992
Ni[S ₂ CN(<i>p</i> -MePhSO ₂)Bz] ₂	<i>E</i> * (kJ mol ⁻¹)	90.6	94.5
	<i>Z</i> (s ⁻¹)	1.41 × 10 ⁷	3.69 × 10 ⁷
	<i>r</i>	0.898	0.989

not [13]. Thus, the decomposition equation for a first-order reaction, i.e. when $n = 1$, of the type $A(s) \rightarrow B(s) + C(g)$, is

$$-\log\left[\frac{-\ln(1-\alpha)}{T^2}\right] = Ze^{-E^*/RT} \quad (1)$$

where α is the degree of decomposition, and

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = Ze^{-E^*/RT} \quad (2)$$

when the order of reaction $n \neq 1$. The reaction order may be determined by employing the Freeman–Carroll equation [10] in the form

$$\frac{\Delta \log(dw/dt)}{\Delta \log w_r} = \frac{(-E^*/2.303R) \Delta(T^{-1})}{\Delta \log w_r} + n \quad (3)$$

where w_r is the total weight loss at temperature T or time t .

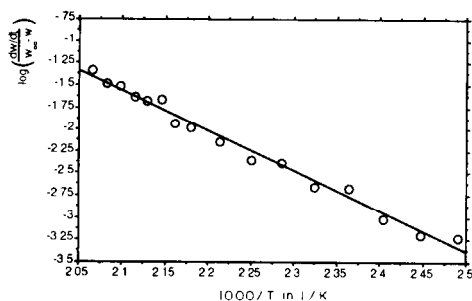


Fig. 4. Freeman–Carroll (modified) plot for $\text{Ni}[\text{S}_2\text{CN}(\text{Ph}_2\text{NCO})\text{Me}]_2$.

The near-unity values of the order of reaction derived from the above analysis of TG data show that first-order kinetics are applicable in all cases. Therefore, by combining the usual first-order rate law expression with the Arrhenius equation, we get

$$\log\left(\frac{dw/dt}{w_x - w}\right) = \frac{-E^*}{2.303RT} + \log Z \quad (4)$$

where w_x is the weight loss at the completion of the reaction, and w the weight loss up to time t .

However, 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 [14, 15]. 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 [16], and for this the integral method of Coats and Redfern [11] was chosen. Accordingly, for first-order processes, eqn.

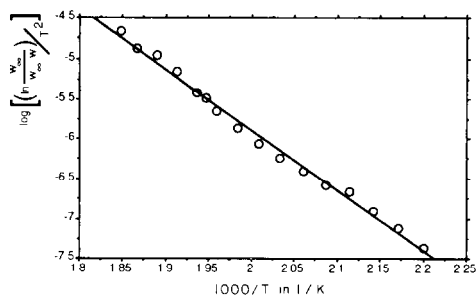


Fig. 5. Coats–Redfern plot for $\text{Ni}[\text{S}_2\text{CN}(\text{COOEt})\text{Bu}^n]_2$.

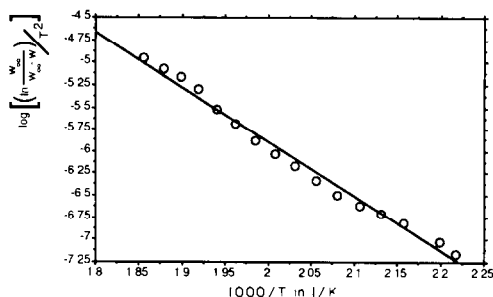


Fig. 6. Coats–Redfern plot for $\text{Ni}[\text{S}_2\text{CN}(\text{PhSO}_2)\text{Me}]_2$.

(1) may be written in the form

$$\log \frac{2.303 \log \left(\frac{w_\infty}{w_\infty - w} \right)}{T^2} = \log \frac{ZR}{\Phi E^*} \left[1 - \frac{2RT}{E^*} \right] - \frac{E^*}{2.303RT} \quad (5)$$

where Φ is the rate of heating.

The kinetic parameters obtained by the application of eqns. (4) and (5) to TG traces are summarized in Table 3. Typical curves are given in Figs. 4–6. All linear plots were evaluated by a regression analysis and the corresponding correlation coefficients (r) were calculated. It follows from the calculated kinetic parameters that the decomposition of the title compounds is a rather low energy process as compared to that of the analogous metal(II) dithiocarbamates [7–9]. However, the activation energies were found to be between 94 and 194 kJ mol^{-1} , and thus comparable with the values previously reported for the nickel(II) amide *N*-carbodithioates [6].

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