

Thermal behaviour and kinetic analysis of the thermogravimetric data of some copper(II), nickel(II), and palladium(II) 2-hydroxyaryloximates

M. Lalia-Kantouri * and M. Hartophylles

Faculty of Chemistry, Department of General and Inorganic Chemistry, University of Thessaloniki, 54006 Thessaloniki (Greece)

(Received 8 January 1993; accepted 8 February 1993)

Abstract

The thermal stability and mode of decomposition of eleven 2-hydroxyaryloxime chelates with the transition metals Cu(II), Ni(II), and Pd(II) have been studied in air atmosphere using the TG/DTA technique. In the case of copper chelates, their thermal behaviour was also studied in nitrogen atmosphere by TG/DTG.

A kinetic analysis of the TG data was performed using the Coats–Redfern method to determine the apparent activation energies and the pre-exponential factor of the Arrhenius equation. Mass spectrometry was also used and possible fragmentation patterns are given and discussed.

INTRODUCTION

Hydroxyoximates constitute a class of organo-nitrogen, oxygen compounds with strong binding properties which are also known to have significant and extensive applications as analytical reagents in solvent extraction systems [1–3] and in hydrometallurgy [4–6]. Such applications are of continuing interest and industrial importance. Moreover, the new application of copper(II) chelates of salicylaldoxime and related ligands as anti-proliferative and anti-neoplastic agents [7, 8] suggests further investigations on the coordination chemistry of hydroxyoximates. In this respect, we have already studied several transition metal complexes of aromatic hydroxyoximes to establish the chemical, electronic and redox properties of the various coordination geometries obtainable within the oxime system [9, 10]. Our results were found to be in accordance with well-established, X-ray structural determinations of the trans square-planar geometry of some salicylaldoximates [11–13].

The thermal behaviour of several divalent metal salicylaldoximates has

* Corresponding author.

received considerable attention from some investigators. Duval [14] and Lumme [15] described the pyrolysis of the chelates with the divalent metals Cu, Ni, Zn, Cd and Pb, focusing their attention on the initial decomposition temperatures and the temperatures at which the metal oxide was formed. Lumme and Korvola [16] studied thermogravimetrically the chelates with Co(II), Ni(II) and Cu(II), and concluded that monosalicylaldoximates were formed as intermediates. They also studied the mass spectra of the copper and nickel chelates and proposed two main decomposition routes involving initially the radical NO and one water molecule or one ligand molecule from the molecular ion. Recently, Lumme and Knuutila [17] studied the thermal decomposition of cadmium and lead bis- and monosalicylaldoximates. The elimination of one ligand molecule from the bisalicylaldoximate was confirmed for the lead chelate only. In addition, they suggested a trans structure for the cadmium chelate and a cis structure for the lead chelate.

We report here the results concerning mass spectral and thermogravimetric studies for complexes with the general formula ML_2 where M is Cu(II), Ni(II), or Pd(II) and L is the anion of the following hydroxyaryloximes: 2-OH, $C_6H_4CR=NOH$ (R is CH_{23} (Hapox), C_2H_5 (Hppox), C_6H_5 (Hbpox)), 2-OH,5-Me, $C_6H_3C(CH_3)=NOH$ (Hmpox), or 2-OH,4-MeO, $C_6H_3C(C_6H_5)=NOH$ (Hopox).

Kinetic parameters (activation energy E^* , pre-exponential factor Z and reduction order n) for the main decomposition stage, derived by the Coats–Redfern method [18], are also reported and discussed.

EXPERIMENTAL

Preparation of samples

Samples of bis(2-hydroxyaryloximato) complexes were prepared from the reaction between the metal(II) chloride (5 mmol) dissolved in water and the appropriate amount of an ethanolic solution of the oxime (10 mmol) as previously reported [9, 10]. Recrystallization was carried out by dissolving the solid in $CHCl_3$ and reprecipitating with ether.

Instrumental

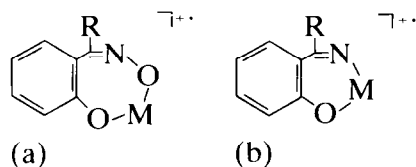
Mass spectra were run at 70 eV on an RMU-6L Hitachi Perkin–Elmer single-focusing mass spectrometer, using direct probe insertion for the samples. The ionization source used was a T-2p model. The TG/DTA curves were obtained on a Rigaku-Denki model 8076-D1 thermal analyser. Samples were heated in platinum crucibles using $\alpha-Al_2O_3$ as a reference compound, in a static air atmosphere within the temperature range 25–800°C. The heating rate was 10°C min⁻¹ and the sample sizes ranged in mass from 12 to 17 mg. X-ray powder diffraction analyses of the final

residues were made with a Philips PW 1130/00 X-ray diffractometer, using Cu K α radiation. For copper chelates, TG/DTG curves were also obtained in dynamic nitrogen atmosphere on a Du Pont Instrument Series 99 thermal analyser with a combined apparatus Du Pont Instrument Series 951 thermogravimetric analyser.

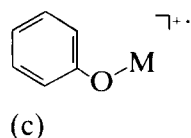
RESULTS AND DISCUSSION

Mass spectral studies

In all the mass spectra recorded, the molecular ion peaks of the chelates (M^+) with relative intensities including the abundance ratio of the metals were detected ($^{63}\text{Cu}:^{65}\text{Cu} = 2.25:1.00$, $^{58}\text{Ni}:^{60}\text{Ni} = 2.59:1.00$, $^{104}\text{Pd}:^{105}\text{Pd}:^{106}\text{Pd}:^{108}\text{Pd}:^{110}\text{Pd} = 1.00:2.03:2.49:2.43:1.08$). The most prominent mass spectral peaks of the studied components are given in tabular form in Table 1 and a general schematic representation including the main fragmentation processes for the copper chelates is given in bar-graph form in Fig. 1. The most intense peaks of each spectrum are those corresponding to the released oxime and its daughter fragments following well-known pathways [16, 17, 19]. The most important higher mass number ions observed in the chelates with copper(II) and nickel(II) correspond to the general formulae



These might be regarded as direct fragments of the molecular ions. The formation of the (a) type ions are accounted for by the rupture of the M–N and M–O coordination bonds and the elimination of the one-ligand molecule. The simultaneous or successive elimination of one water molecule along with the evolved ligand leads to the formation of the (b) type ions. From these ions, elimination of the groups RCNO or RCN, respectively, leads to the formation of the ion with the general formula



which finally fragments to yield the metal. A simplified picture of the main fragmentation pathways for the propiophenoneoximates with the studied metals is presented in Scheme 1. The formation of the ions (a), (b) and (c) is demonstrated by the pathways Ia and Ib.

TABLE 1

The most relevant mass spectral peaks of some 2-hydroxyaryloximates

Complex	<i>m</i> /(<i>RI</i>) ^a
Cu(apox) ₂	18(23), 41(11), 63(39), 65(28), 77(20), 91(100), 92(41), 105(97), 119(22), 133(63), 134(17), 135(21), 151(23), 153(7), 155(4), 196(15), 198(8), 211(10), 213(4), 363(12), 365(5)
Cu(mpox) ₂	18(78), 28(100), 41(41), 57(24), 63(15), 65(11), 72(22), 92(7), 105(22), 147(15), 155(11), 157(5), 165(12), 167(4), 169(5), 228(2), 230(1), 393(2), 395(1)
Cu(ppox) ₂	55(4), 63(19), 65(13), 77(8), 91(48), 92(10), 119(100), 147(30), 148(29), 149(16), 165(32), 209(44), 211(21), 225(11), 227(7), 391(16), 393(8)
Cu(bpox) ₂	63(86), 65(46), 75(39), 77(100), 92(69), 103(76), 119(14), 155(6), 157(2), 167(100), 195(100), 196(100), 211(18), 212(7), 213(95), 214(15), 257(2), 259(1), 273(2), 275(1), 487(2), 489(1)
Ni(apox) ₂	41(19), 55(100), 58(17), 60(7), 77(9), 91(5), 92(26), 105(14), 119(8), 133(7), 134(19), 135(7), 149(12), 150(6), 152(14), 155(15), 192(22), 194(9), 208(28), 209(8), 358(42), 360(16)
Ni(mpox) ₂	18(21), 28(100), 41(40), 55(49), 57(31), 77(11), 105(15), 147(7), 150(5), 151(8), 152(3), 155(11), 165(8), 167(3), 204(3), 206(1), 220(3), 222(1), 386(4), 388(2)
Ni(ppox) ₂	55(7), 58(16), 60(6), 77(7), 91(19), 92(7), 119(28), 147(6), 148(37), 149(15), 150(6), 152(2), 165(14), 167(3), 204(34), 206(14), 220(3), 222(1), 386(100), 388(60)
Ni(bpox) ₂	57(19), 63(29), 75(14), 77(86), 92(17), 103(97), 119(26), 149(26), 152(14), 167(67), 195(100), 196(62), 213(45), 252(3), 254(1), 268(2), 270(1), 482(12), 484(5)
Pd(apox) ₂	41(17), 77(11), 91(100), 92(17), 104(8), 105(38), 106(11), 108(9), 110(5), 119(27), 121(6), 133(30), 134(23), 135(18), 149(11), 151(23), 152(21), 195(6), 196(10), 197(16), 198(9), 199(16), 201(7), 203(5), 223(5), 224(9), 225(11), 227(9), 229(3), 240(5), 254(3), 255(6), 257(5), 374(4), 375(7), 376(10), 378(8), 380(5), 404(7), 405(15), 406(21), 408(19), 410(8)
Pd(mpox) ₂	18(100), 28(79), 77(39), 104(21), 105(29), 133(18), 147(29), 165(29), 403(10), 404(16), 406(14), 408(7), 432(21), 433(36), 434(50), 436(43), 438(18)
Pd(ppox) ₂	28(100), 77(30), 91(57), 92(13), 104(13), 105(63), 106(17), 108(13), 110(9), 119(52), 133(72), 196(5), 197(9), 198(13), 200(11), 202(7), 222(3), 223(5), 224(8), 226(8), 228(4), 237(33), 238(50), 239(67), 241(57), 243(24), 250(3), 251(5), 252(7), 254(7), 256(4), 266(3), 267(5), 271(4), 402(9), 403(17), 404(22), 406(20), 408(9), 432(28), 433(60), 434(82), 436(69), 438(33)
Pd(bpox) ₂	28(100), 77(41), 104(3), 105(5), 106(8), 108(7), 110(4), 119(6), 167(36), 181(8), 195(36), 196(16), 197(7), 199(6), 213(21), 285(1), 286(2), 287(4), 289(2), 291(1), 528(1), 529(2), 530(3), 532(2), 534(1)

^a Relative intensity.

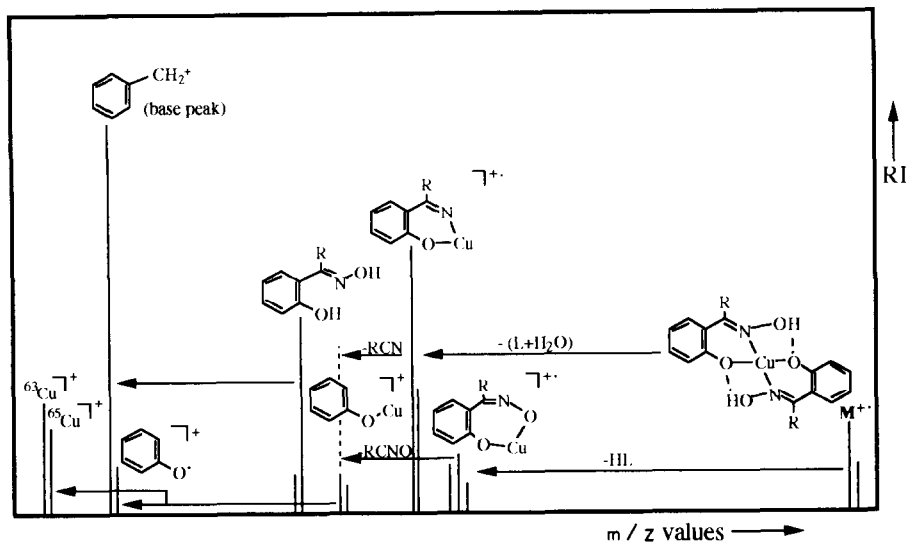
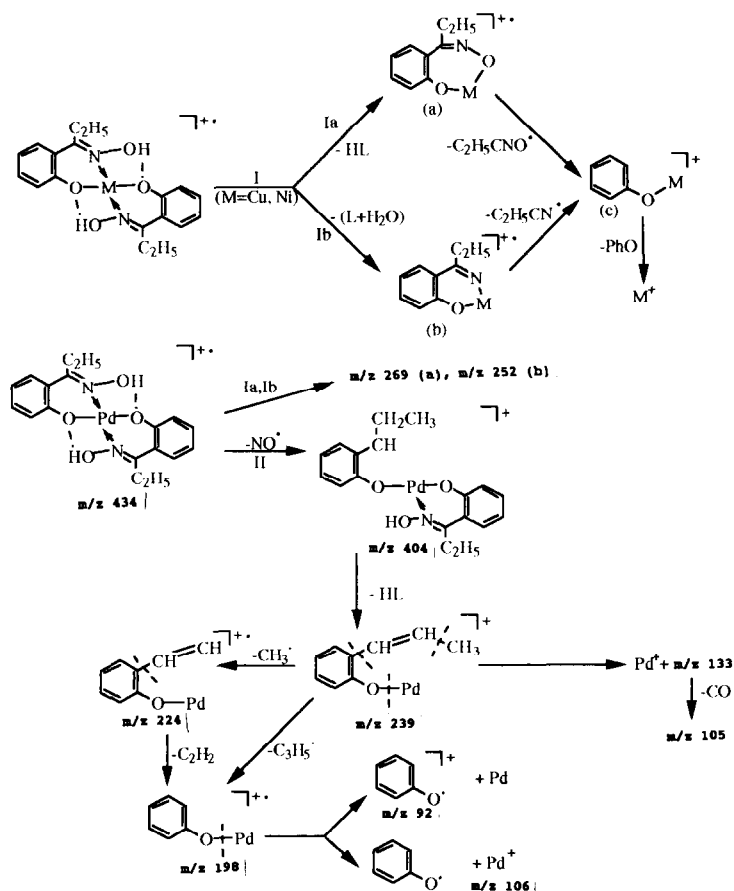
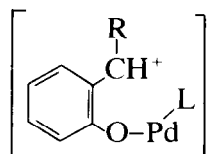


Fig. 1. Schematic representation of the general fragmentation pattern of copper hydroxyaryloximates.



Scheme 1. Possible fragmentation patterns of the $M(ppox)_2$ complexes.

The observed fragment ions in the mass spectra of the palladium chelates correspond mostly to the general formula



(d)

and might be regarded as a direct fragment of the molecular ion by the expulsion of nitrogen monoxide. This ion is further fragmented following different pathways depending on the oxime ligand.

The fragment ions corresponding to pathway I found for the copper(II) and nickel(II) chelates, have also been observed for Pd(II) complexes but with weaker relative intensities.

Thermal behaviour

All of the complexes were subjected to TG/DTA analysis from ambient temperature to 800°C in static air atmosphere. Typical thermoanalytical curves for copper(II), nickel(II) and palladium(II) 2-hydroxyaryloximates are presented in Fig. 2, while the temperature ranges, determined percentage weight losses, and thermal effects accompanying the decomposition reactions, for all complexes are given in Table 2.

The DTA curve shapes indicate that for the copper(II) chelates, melting seems to take place just before decomposition, as indicated by small endothermic peak just preceding the exothermic one, while for some nickel(II) and all the palladium chelates, decomposition takes place without melting. For all the complexes studied, the degradation stages are accompanied by exothermic effects.

The studied complexes decompose in two or three stages depending on the metal and the ligand. In general, decomposition begins between 200 and 265°C for copper(II), 320–350°C for nickel(II) and 340–370°C for Pd(II) complexes, which means that the thermal stability of the complexes with the same ligand decreases in the order Pd > Ni > Cu. This series is in agreement with what Seshagiri and Brahmaji Rao found for the thermal stability of resacetophenoneoximates with the same metals, with the solution stability of the chelates being in the reverse order [20]. For complexes with the same metal, the thermal stability follows the series opox > bpox > mpox > apox > ppox, which is in agreement with the thermal stability of the free ligands.

The free ligands are less stable than the analogous complexes, losing

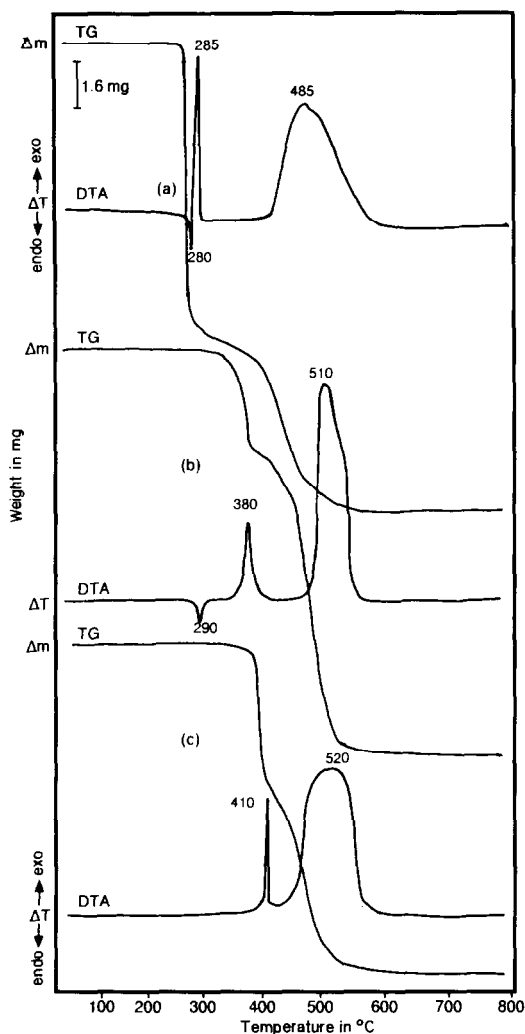


Fig. 2. Thermoanalytical curves of (a) $\text{Cu}(\text{apox})_2$, (b) $\text{Ni}(\text{ppox})_2$ and (c) $\text{Pd}(\text{bpox})_2$ in air.

about 91% of their weight in one stage. This main decomposition stage is followed by a final weight loss occurring at around 500°C and leaving an empty crucible at about 700°C.

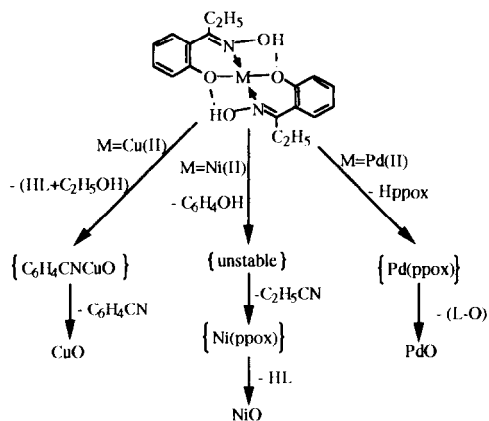
The thermal decomposition mode of the investigated compounds does not follow a definite model. Scheme 2 indicates the proposed stages of the thermal degradation of propiophenoneoximates which are the most frequently observed reaction paths, derived from the TG/DTA curves. The theoretical weight losses are consistent with the observed values in each particular transition stage; the intermediates are unstable and undergo further decomposition until a stable metal oxide is formed at about 550°C verified from the X-ray powder diffraction data. Where possible, the

TABLE 2
Thermoanalytical results (TG/DTA) for copper(II), nickel(II) and palladium(II) 2-hydroxyaryloximates in air

Compound	Stage	Temperature range/°C	DTA	Endo (-) Exo (+)		Mass loss/ %	Evolved moiety formula	Mass calc./ %
				Endo (-)	Exo (+)			
Cu(apox) ₂	1	260-300	280	285		50.3	L + CH ₃ OH	50.3
	2	300-580		485		27.9	C ₆ H ₄ CN	28.0
	Residue >580°C					21.9	CuO	21.8
Cu(mpox) ₂	1	240-295	285	290		38.0	CH ₃ CNO + CH ₃ C ₆ H ₅	37.6
	2	295-520		350, 370, 430		42.0	HL	42.1
	Residue >520°C					20.0	CuO	20.3
Cu(ppox) ₂	1	220-300	270	280		52.5	L + C ₂ H ₅ OH	53.5
	2	300-560		520		57.5	C ₆ H ₄ CN	26.2
	Residue >560°C					20.0	CuO	20.3
Cu(bpox) ₂	1	265-310	305	310		24.8	PhCNO	24.8
	2	310-420		400		21.4	PhCN	21.1
	3	420-620		560		36.8	2PhO	37.7
	Residue >620°C					17.0	CuO	16.3
Cu(opox) ₂	1	200-295		295		17.2	PhOH	17.0
	2	295-440		370, 420		36.3	PhCNO + Ph	35.8
	3	440-600		560		32.5	CH ₃ OC ₆ H ₃ OCN + OCH ₃	32.7
	Residue >600°C					14.0	CuO	14.5

Ni(ppox) ₂	1	320-400	290	380	23.6	C ₆ H ₄ OH	24.0
	2	400-460			13.5	C ₂ H ₅ CN	14.1
	3	460-540		510	43.6	HL	42.6
	Residue >540°C				19.3	NiO	19.4
Ni(npox) ₂	1	340-380	260	360	19.3	PhOH	19.2
	2	380-550		560	65.7	L + PhCN	65.2
	Residue >55°C				15.0	NiO	15.5
Ni(opox) ₂	1	350-420	310	370	17.0	PhOH	17.3
	2	370-560		560	69.8	L + CH ₃ OC ₆ H ₅ CN	68.9
	Residue >560°C				13.2	NiO	13.8
Pd(ppox) ₂	1	340-420	305	390, 405	37.7	HL	37.9
	2	420-620	445	560b	34.7	L-O	34.0
	Residue >620°C				27.6	PdO	28.2
Pd(bpox) ₂	1	360-460		410	40.2	HL	40.1
	2	460-560		520	37.6	L-O	36.9
	Residue >560°C				22.2	PdO	23.1
Pd(opox) ₂	1	370-430	395	410	40.3	HL	41.0
	2	430-500		470	39.7	L-O	38.3
	Residue >500°C				20.0	PdO	20.7

Key: b means broad.



Scheme 2. Proposed thermal decomposition routes for the $M(\text{ppox})_2$ complexes.

intermediates were deduced by elemental analyses, and mass and IR spectra.

The decomposition of palladium compounds proceeds with rupture of the coordination bonds by the elimination of one oxime molecule in the first stage, while for the nickel compounds the decomposition begins by the rupture of the bonds inside the ligands. In the case of some copper compounds, however (Table 2), the first stage includes ruptures of both the coordination bonds and of bonds inside the ligand. In general, the thermal decomposition modes of the studied compounds are in fair agreement with the fragmentation patterns derived from their mass spectra, any differences being due to the different conditions in the ionization chamber.

Thermogravimetric studies (TG/DTG) over the temperature range 50–750°C were also carried out in nitrogen for the copper complexes. Representative thermal curves for $\text{Cu}(\text{opox})_2$ are given in Fig. 3 and the thermoanalytical data derived from the thermal curves are presented in Table 3. The decomposition processes of the complexes include various thermal effects and do not always follow the same pathways as in air. In nitrogen, the thermal degradation of the complexes leads to a thermally unstable residue at 750°C which consists of a mixture of CuO and some ligand residue, as confirmed by the IR spectra.

Decomposition kinetics

The first stage of decomposition in air for some of the complexes under investigation was chosen for detailed study. The kinetic parameters (activation energy E^* , reaction order n and pre-exponential factor Z) were evaluated graphically by employing the Coats–Redfern equation

$$\log \frac{(1 - (W_a - W/W_a))^{1-n}}{(1-n)T^2} = \log \frac{ZR}{\Phi E^*} \left(1 - \frac{2RT}{E^*}\right) - \frac{E^*}{2.303RT} \quad (1)$$

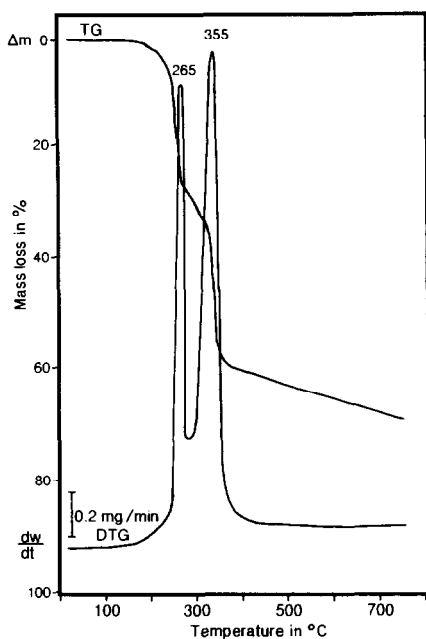


Fig. 3. Thermoanalytical curves of $\text{Cu}(\text{opox})_2$ in nitrogen.

where W_a is total mass loss in the first stage, Φ the rate of heating, R the molar gas constant, T the temperature, n the reaction order ($\neq 1$) and Z the frequency factor representing the total frequency encounters between two reactant molecules.

TABLE 3

Thermoanalytical results (TG/DTG) for copper(II) 2-hydroxyaryloximates in nitrogen

Compound	Stage	Temperature range/°C	DTG _{max} /°C	Mass loss/%	Evolved moiety formula	Mass calc./%
$\text{Cu}(\text{apox})_2$	1	230–310	265	42.5	HL	41.5
	2	310–650	–	15.5	CH_3CNO	15.7
	Residue	750	–	37.0	$\text{CuO} + \text{X}$	$21.8 + \text{X}$
$\text{Cu}(\text{mpox})_2$	1	240–310	260	30.0	$2\text{CH}_3\text{CNO}$	29.1
	2	310–690	–	27.0	CH_3PhO	27.6
	Residue	750	–	40.0	$\text{CuO} + \text{X}$	$20.3 + \text{X}$
$\text{Cu}(\text{ppox})_2$	1	220–310	252	52.5	$\text{L} + \text{C}_2\text{H}_5\text{OH}$	53.5
	2	310–650	–	7.9	HCN	6.9
	Residue	750	–	37.0	$\text{CuO} + \text{X}$	$20.3 + \text{X}$
$\text{Cu}(\text{bpox})_2$	1	130–200	200	9.2	NO_2	9.4
	2	250–300	280	42.8	L–O	41.3
	3	300–450	350	19.7	PhCN	20.7
	Residue	750	–	25.0	$\text{CuO} + \text{X}$	$16.3 + \text{X}$
$\text{Cu}(\text{opox})_2$	1	160–275	265	23.0	PhCNO	21.7
	2	275–400	355	32.5	$\text{PhCNO} + 2\text{CH}_3\text{O}$	33.0
	Residue	750	–	35.0	$\text{CuO} + \text{X}$	$14.5 + \text{X}$

TABLE 4

Kinetic data for some 2-hydroxyaryloximates

Compound	Evolved group	$E^*/$ (kJ mol ⁻¹)	Z/s^{-1}	r^a
Cu(ppox) ₂	HL + C ₂ H ₅ OH	196	1.13×10^{14}	0.986
Cu(opox) ₂	PhOH	132	3.80×10^{12}	0.990
Ni(ppox) ₂	PhOH	274	4.38×10^{16}	0.992
Ni(bpox) ₂	PhOH	261	8.23×10^{14}	0.994
Pd(ppox) ₂	HL	215	1.44×10^{11}	0.986
Pd(bpox) ₂	HL	198	1.02×10^{15}	0.996
Hppox		93	9.06×10^1	0.992
Hbpox		72	1.26×10^0	0.986

^a Correlation coefficient of the linear plot.

Because $1 - 2RT/E^* \approx 1$, the left-hand-side of the expression was plotted against $1/T$; E^* was calculated from the slope. This value of E^* was used to calculate Z from the intercept.

The kinetic parameters obtained by the application of eqn. (1) to the thermoanalytical data are summarized in Table 4. A typical curve is given in Fig. 4 for Ni(ppox)₂. All the linear plots were evaluated by a regression analysis, and the corresponding correlation coefficients (r) were calculated. It was found that better linear plots were obtained when the reaction order equals 0.5.

The results reveal that the activation energies for nickel and palladium complexes are in good agreement with our previous reports [21, 22] for nickel and palladium mono-substituted dithiocarbamates. Moreover, if we

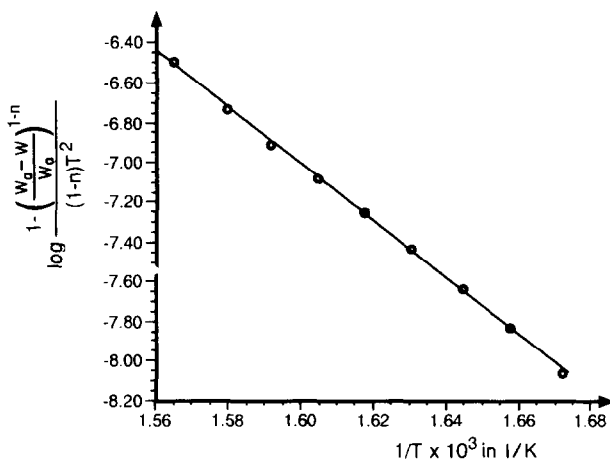


Fig. 4. Coats-Redfern plot for Ni(ppox)₂.

consider complexes with the same ligand and different metals, it can be concluded that the activation energies of the palladium complexes are smaller than those of nickel and copper. This is in agreement with the thermal stability series found for the studied complexes, based on their initial decomposition temperature, as described previously. From Table 4, it is also concluded that the thermal decomposition of the free hydroxyoximes follows a low energetic process.

ACKNOWLEDGEMENTS

The authors express their thanks to Mr. G. Bourboulis, in Tekkosha Hellas, Thessaloniki, for technical assistance.

REFERENCES

- 1 A. Chakravorty, *Coord. Chem. Rev.*, 13 (1974) 1.
- 2 R.B. Singh, B.S. Gag and R.P. Singh, *Talanta*, 26 (1979) 425.
- 3 R.C. Mehrotra, A.K. Singh and R. Bohra, *Inorg. Chim. Acta*, 13 (1975) 91.
- 4 A.W. Ashbrook, *Coord. Chem. Rev.*, 16 (1975) 285.
- 5 J.S. Preston, *J. Inorg. Nucl. Chem.*, 37 (1975) 1235.
- 6 J.M. Pratt and R.I. Tilley, *Hydrometallurgy*, 5 (1979) 29.
- 7 H. Elo and P. Lumme, *Inorg. Chim. Acta*, 136 (1987) 149.
- 8 H. Elo, *Inorg. Chim. Acta*, 136 (1987) L33.
- 9 M. Lalia-Kantouri and M. Hartophylles, *Polyhedron*, 11 (1992) 789.
- 10 M. Lalia-Kantouri et al., unpublished data, 1992.
- 11 L. Merritt, C. Guare and A.E. Lessor, *Acta Crystallogr.*, 9 (1956) 253.
- 12 M.A. Jarski and E.C. Lingafelter, *Acta Crystallogr.*, 17 (1964) 1109.
- 13 C.E. Pfluger, R.L. Harlow and S.H. Simonsen, *Acta Crystallogr. Sect. B*, 26 (1970) 1631.
- 14 C. Duval, *Inorganic Thermogravimetric Analysis*, Elsevier, Amsterdam, 2nd edn., 1963, p. 390, 424, 478, 631, 643.
- 15 P. Lumme, *Suom. Kemistil. B*, 32 (1959) 261.
- 16 P. Lumme and M.L. Korvola, *Thermochim. Acta*, 13 (1975) 419.
- 17 P. Lumme and P. Knuuttila, *J. Therm. Anal.*, 25 (1982) 139.
- 18 A.W. Coats and J.P. Redfern, *Nature*, 201 (1964) 68.
- 19 M. Lozynski and E. Krzyzanowska, *Org. Mass Spectrom.*, 21 (1986) 33.
- 20 V. Seshagiri and S. Brahmaji Rao, *Fresenius, Z. Anal. Chem.*, 262 (1972) 275.
- 21 M. Lalia-Kantouri, G.A. Katsoulos, C.C. Hadjikostas and P. Kokorotsikos, *J. Therm. Anal.*, 35 (1989) 2411.
- 22 G.A. Katsoulos, M. Lalia-Kantouri, C.C. Hadjikostas and P. Kokorotsikos, *Thermochim. Acta*, 149 (1989) 331.