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Kinetic analysis of thermogravimetric data of *p*-toluidino-*p*-chlorophenylglyoxime and of some complexes

Hakan Arslan[a,*], Nilgün Özpozan[b], Necdet Tarkan[a]

[a]*Department of Chemistry, Faculty of Arts and Sciences, Mersin University, Mersin, Turkey*
[b]*Department of Chemistry, Faculty of Arts and Sciences, Erciyes University, Kayseri, Turkey*

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Abstract

Thermogravimetric (TG) and derivative thermogravimetric (DTG) investigations of *p*-toluidino-*p*-chlorophenylglyoxime (*p*-T-*p*-CPG) and of some complexes (Co(II), Ni(II), and Cu(II)) in dynamic nitrogen atmosphere have been studied to determine their modes of decomposition. All the complexes showed similar TG behaviour. The mass losses in the main decomposition stage indicated conversion of the metal complexes to its oxide. A gas chromatography–mass spectrometry (GC–MS) combined system was used to identify the products during pyrolytic decompositions. The final products of the decompositions were identified by X-ray powder diffraction method. The kinetic parameters (energy, entropy of activation and pre-exponential factor) were calculated from the data of TG curves. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: *p*-Toluidino-*p*-chlorophenylglyoxime; Co(II), Ni(II) and Cu(II) complexes; Thermal behaviour; Decomposition kinetics; DTA/TG/DTG

1. Introduction

The importance of coordination compounds in biological systems, their increased uses in industry and the reality that they could be used as anti-tumour agents in chemotherapy have led to an increase in investigations of these complexes, especially the vic-dioxime complexes, which are widely used in analytical chemistry to detect many elements as they are highly selective complexing conformers [1–3]. Today, new vic-dioximes are being synthesised and transition metal complexes are being isolated at an increasing rate.

p-Toluidino-*p*-chlorophenylglyoxime (*p*-T-*p*-CPG) and its Co(II), Ni(II) and Cu(II) complexes have been studied [4] (see Fig. 1). After searching the literature we could not find any thermal decomposition kinetics data of this type of vic-dioximes. In this study, decomposition kinetics were investigated for vic-dioxime complexes and the relation between metal properties (such as radius) and decomposition kinetics data have also been examined. Thermoanalytical data (thermogravimetric (TG), derivative thermogravimetric (DTG) and differential thermal analysis (DTA)) of three typical complexes, i.e. *p*-T-*p*-CPG in this paper, interpretation and mathematical analysis of those data and the energy and entropy of activation, based on the

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[*] Corresponding author. Tel.: +90-532-707-31-22; fax: +90-324-361-00-47.
E-mail address: arslanh@mersin.edu.tr (H. Arslan).

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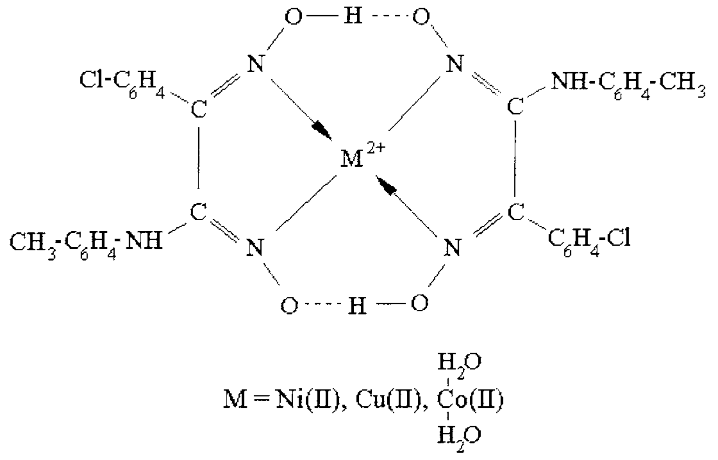

Fig. 1. Octahedral and square-planar metal complexes of the *p*-toluidino-*p*-chlorophenylglyoxime ligand.

integral method using Coats and Redfern equation in [5] and the approximation method using Horowitz and Metzger equation are given in [6].

2. Experimental

2.1. Preparation of samples

p-T-*p*-CPG was synthesised and its complexes with Co(II), Ni(II) and Cu(II) were prepared using a previously described method [7]. All chemicals used were of analytical reagent grade or chemically pure.

2.2. Instrumentation

The thermal studies were carried out on a Shimadzu DT-40 Thermal Analyser with simultaneous DTA–TG module. TG and DTA curves were recorded in a nitrogen furnace atmosphere at a heating rate of $10\,\mathrm{K\,min^{-1}}$ in the temperature range between 273 and 1823 K with samples varying in mass from 4 to 8 mg. α-Al_2O_3 was used as a reference.

Infrared spectra were recorded in the region 4000–$400\,\mathrm{cm^{-1}}$ on a Shimadzu 435 spectrophotometer, using KBr pellets.

X-ray powder diffraction analyses of the final residues were made with a Siemens F model diffractometer. X-ray generator is Phillips PW-1010 model ranging from 20 to 40 kV and from 6 to 50 mA while using fine focus Cu Kα radiation ($\lambda = 1.5406$ Å).

A gas chromatography–mass spectrometry (GC–MS) system VG-ZabSpect model DFMS, was used to identify pyrolysis products evolved during heating.

Melting points were measured using an Electrothermal 9200 model digital melting point apparatus.

3. Results and discussions

The thermal behaviour of the above ligand and complexes have been studied elsewhere in detail [4]. The TG curves were redrawn as % mass loss versus temperature (TG) and also as the rate of loss of mass versus temperature (DTG) curves. Typical TG–DTG and DTA curves are presented in Fig. 2(a)–(c), respectively, and the thermal curves obtainedfor most of the compounds were very similar in character. Thermal data of the compounds are summarised in Table 1 together with the radii of the metal ions.

p-T-*p*-CPG and its Co(II), Ni(II) and Cu(II) complexes are thermal stable up to 401, 408, 453, 383 K, respectively. It was found that pyrolytic decomposition occurs together with melting in both ligand and its metal complexes. The ligand decomposes in two stages and the metal complexes undergo decomposition in three stages through different mechanisms (see Table 1).

Cu(II) and Ni(II) complexes which have a square-planar structure undergo similar thermal decomposition in three stages and produce metal oxides (NiO and CuO). Co(II) complexes which have an octahedral coordination undergo decomposition in three stages and turn to CoO but yield different intermediate products. X-ray powder diffraction data, GC–MS data and TG data confirm our obtained results.

Ni(II) and Cu(II) complexes produce $CH_3C_6H_4NHCN + 2OH + NO$ substances at the first stage whereas Co(II) complexes produce $CH_3C_6H_4$ $NHCN + 2H_2O$. At the second stage, Ni(II)

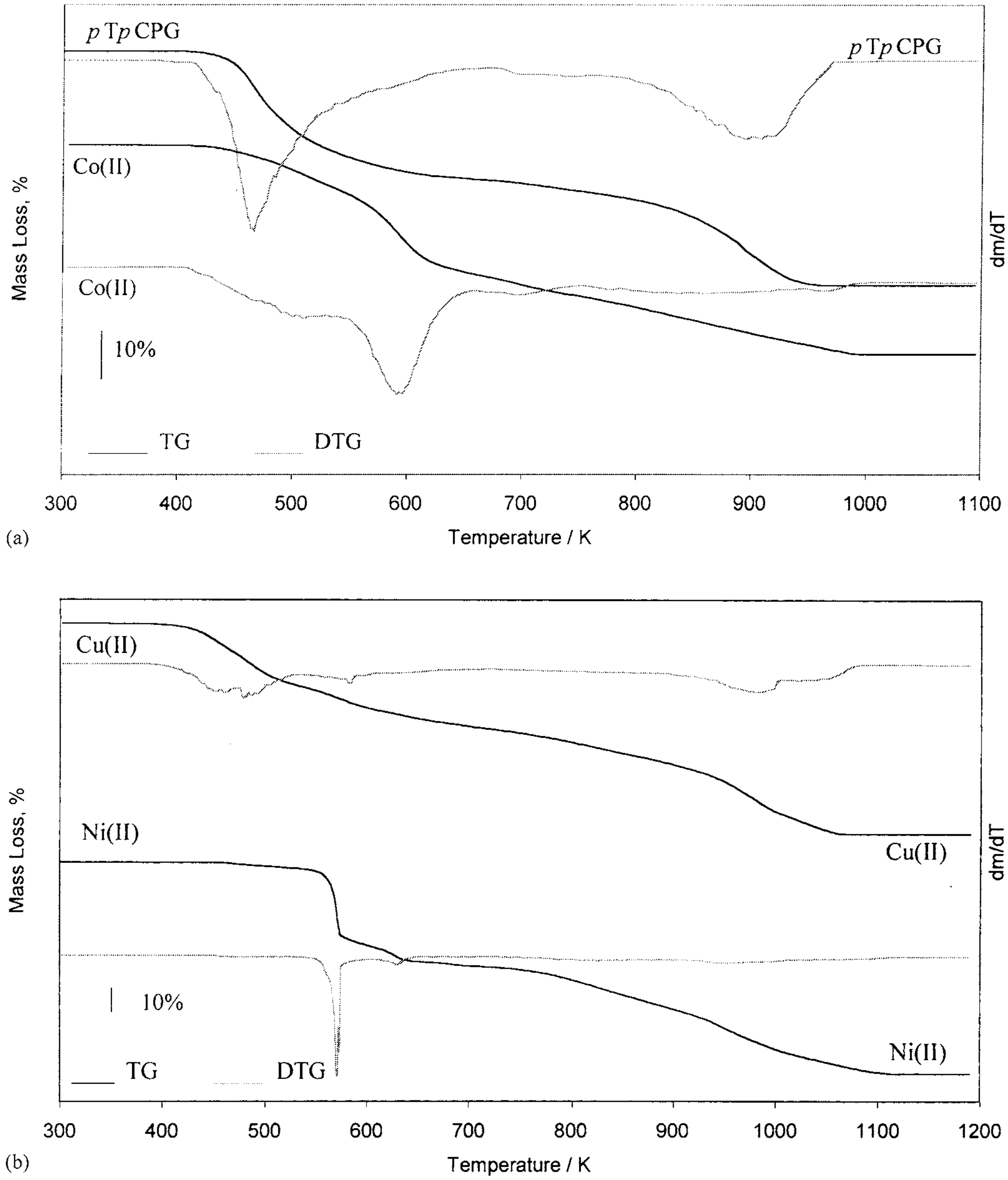

Fig. 2. (a) TG–DTG curves of *p*-toluidino-*p*-chlorophenylglyoxime ligand and its Co(II) complex; (b) TG–DTG curves of Ni(II)– and Cu(II)–*p*-toluidino-*p*-chlorophenylglyoxime complexes; (c) DTA curves for *p*-toluidino-*p*-chlorophenylglyoxime ligand and Co(II)–, Ni(II)–, Cu(II)–*p*-toluidino-*p*-chlorophenylglyoxime complexes.

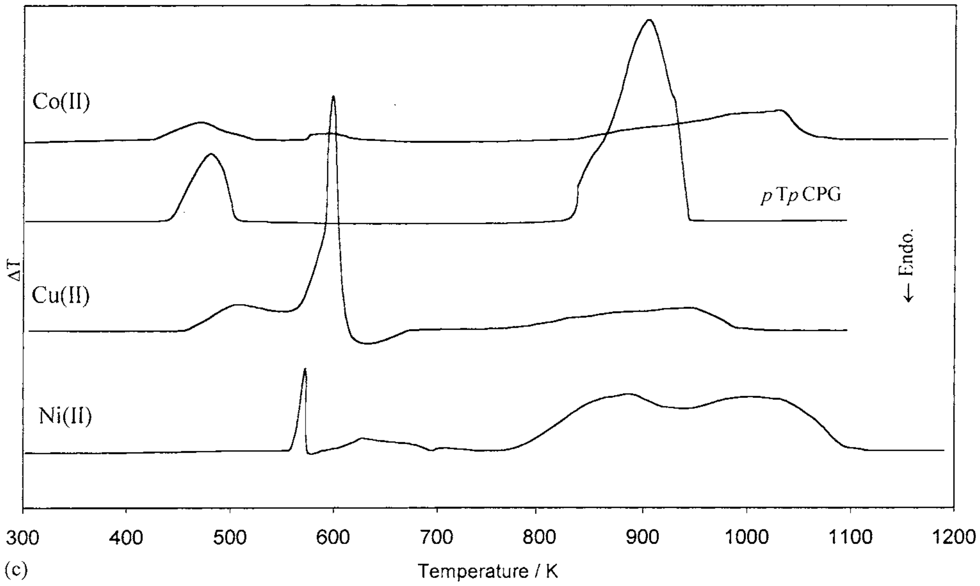

Fig. 2. (*Continued*).

and Cu(II) complexes yield $CH_3C_6H_4NCH$ whereas Co(II) complexes yield $CH_3C_6H_4NCH + 2OH + NO$. At the last stage, the product (ClC_6H_4CN) is the same for all these complexes. These results were confirmed by TG data, GC–MS analysis data ($CH_3C_6H_4NHCN$ (133 *m*/*z*), $CH_3C_6H_4NCH$ (118 *m*/*z*), ClC_6H_4CN (137 *m*/*z*)) and micro-analysis data (found: C 54.6%, H 3.6%; N 13.0%; $C_{30}H_{26}N_6O_4Cl_2Ni$ requires: C 54.3%, H 3.9%; N 12.7%; found: C 53.5%; H 3.6%; N 12.3%; $C_{30}H_{26}N_6O_4Cl_2{\cdot}Cu$ requires: C 53.9%, H 3.9%; N 12.6%; found: C 51.2%; H 4.3%; N 12.2%; $C_{30}H_{26}N_6O_4Cl_2Co{\cdot}2H_2O$ requires: C 51.4%; H 4.3%; N 12.0%; found: C 59.3%; H 4.7%; N 13.9%; $C_{15}H_{14}N_3O_2Cl$ requires: C 59.3%; H 4.6%;

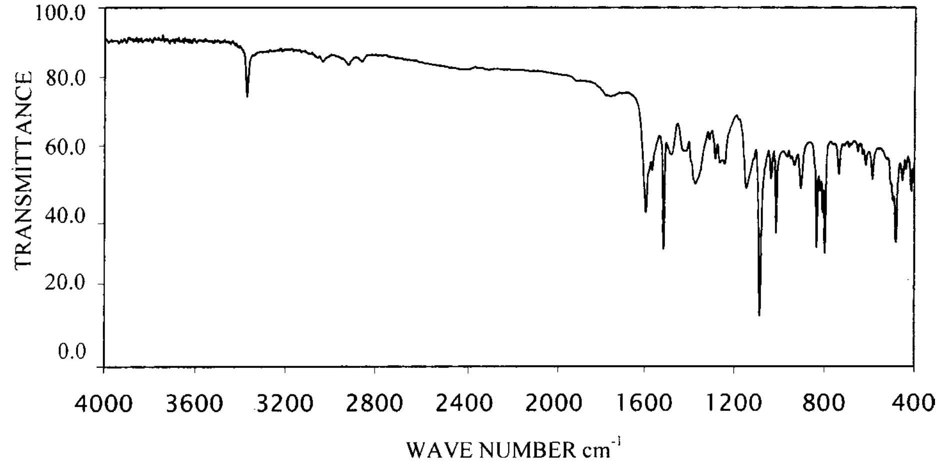

Fig. 3. IR spectra of Ni(II)-*p*-toluidino-*p*-chlorophenylglyoxime complex.

Table 1
Thermal decomposition data and radii of metal ions

Sample	Radius of metal ion (pm)	Stage	TG results temperature range (K)	DTG results temperature peak (K)	DTA results temperature peak (K)	Weight loss (%)		Evolved moiety	Stage products
						Found	Calculated		
p-T-*p*-CPG	–	I	401–669	467	481	55.12	54.71	$CH_3C_6H_4NHCN + 2OH$	ClC_6H_4CN
		II	669–973	908	903	44.85	45.29	ClC_6H_4CN	–
Cu(*p*-T-*p*-CPG)$_2$	70	I	383–567	487	470	30.34	29.32	$CH_3C_6H_4NHCN + 2OH + NO$	$[C_{22}H_{16}N_3OCl_2]\cdot Cu$
		II	567–770	583	592	16.65	17.66	$CH_3C_6H_4NCH$	$[C_{14}H_8N_2OCl_2]\cdot Cu$
		III	770–1080	986	1034	41.11	41.13	$2ClC_6H_4CN$	CuO
		Residue	>1080			11.90	11.89	–	CuO
Ni(*p*-T-*p*-CPG)	72	I	453–575	571	571	30.77	29.54	$CH_3C_6H_4NHCN + 2OH + NO$	$[C_{22}H_{16}N_3OCl_2]\cdot Ni$
		II	575–786	631	624	16.68	17.79	$CH_3C_6H_4NCH$	$[C_{14}H_8N_2OCl_2]\cdot Ni$
		III	786–1111	961	889–1006	40.81	41.42	$2ClC_6H_4CN$	NiO
		Residue	>1111	–	–	11.74	11.25	–	NiO
Co(*p*-T-*p*-CPG)$_2\cdot 2H_2O$	74	I	408–557	509	506	23.56	24.01	$CH_3C_6H_4NHCN + 2H_2O$	$[C_{22}H_{18}N_4O_4Cl_2]\cdot Co$
		II	557–617	591	599	25.51	26.01	$CH_3C_6H_4NCH + 2OH + NO$	$[C_{14}H_8N_2OCl_2]\cdot Co$
		III	617–996	968	947	39.93	39.28	$2ClC_6H_4CN$	CoO
		Residue	>996	–	–	11.00	10.70	–	CoO

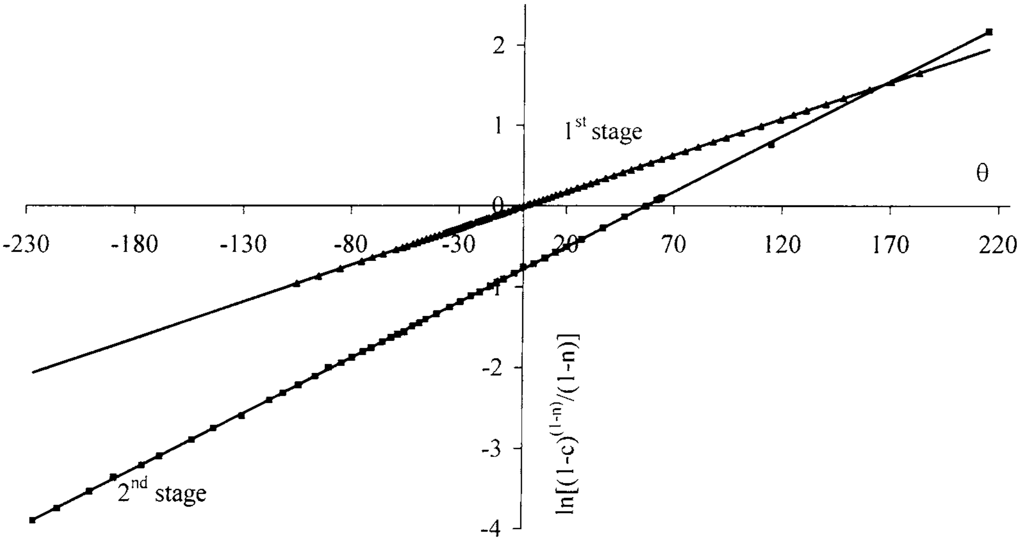

Fig. 4. Linearisation curves of Horowitz and Metzger method for *p*-toluidino-*p*-chlorophenylglyoxime ligand.

N 13.8%). By considering the mass loss of the complexes and X-ray diffraction data [8] the final products was indicated to be oxide (NiO, CuO and CoO).

It has been noticed that molecules except Co(II) complex did not contain any hydrate molecules according to the IR measurements (see Fig. 3). As additional evidence there is no dedectable change in TG curves up to 100 °C. These results were confirmed by CHN analysis for all compounds.

From the TG curves, the order *n*, activation energy E^*, entropies ΔS^*, and pre-exponential factor *A* of the thermal decomposition have been elucidated by the methods of Coats and Redfern and Horowitz and Metzger [5,6].

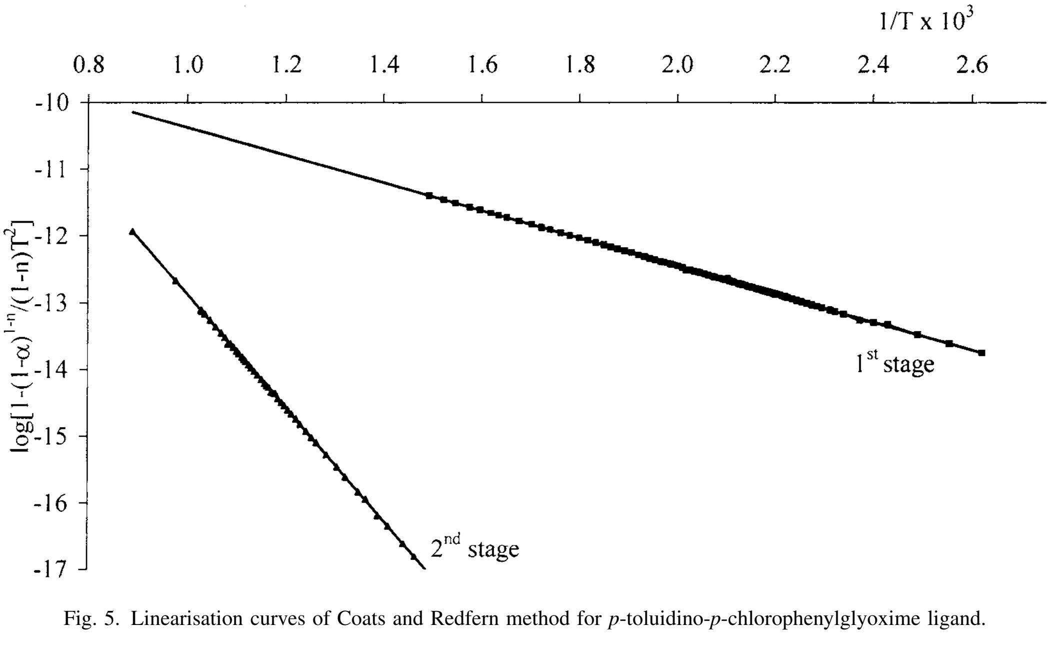

Fig. 5. Linearisation curves of Coats and Redfern method for *p*-toluidino-*p*-chlorophenylglyoxime ligand.

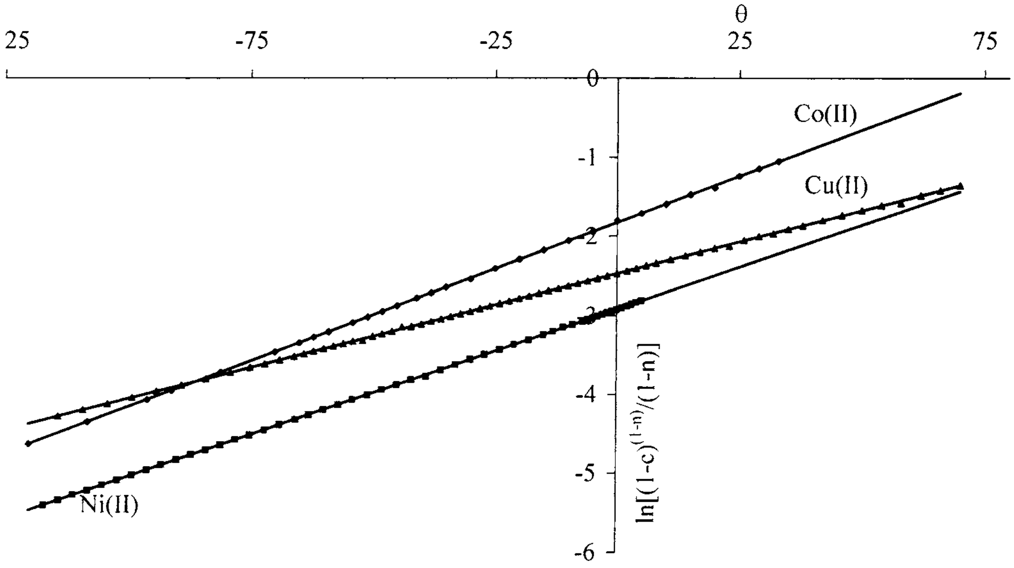

Fig. 6. Linearisation curves of Horowitz and Metzger method for Co(II)–, Ni(II)–, and Cu(II)-*p*-toluidino-*p*-chlorophenylglyoxime complexes.

The linearisation curves of ligand that are obtained by Horowitz and Metzger and Coats and Redfern are presented in Figs. 4 and 5, respectively. And the complex curves which obtained by Horowitz and Metzger and Coats and Redfern are presented in Figs. 6 and 7, respectively. The results of kinetic studies of TG–DTG are presented in Table 2.

The value of correlation coefficients of linearisation curves of ligand and its complexes are approximately 1. And their reaction orders are 1 for ligand and about

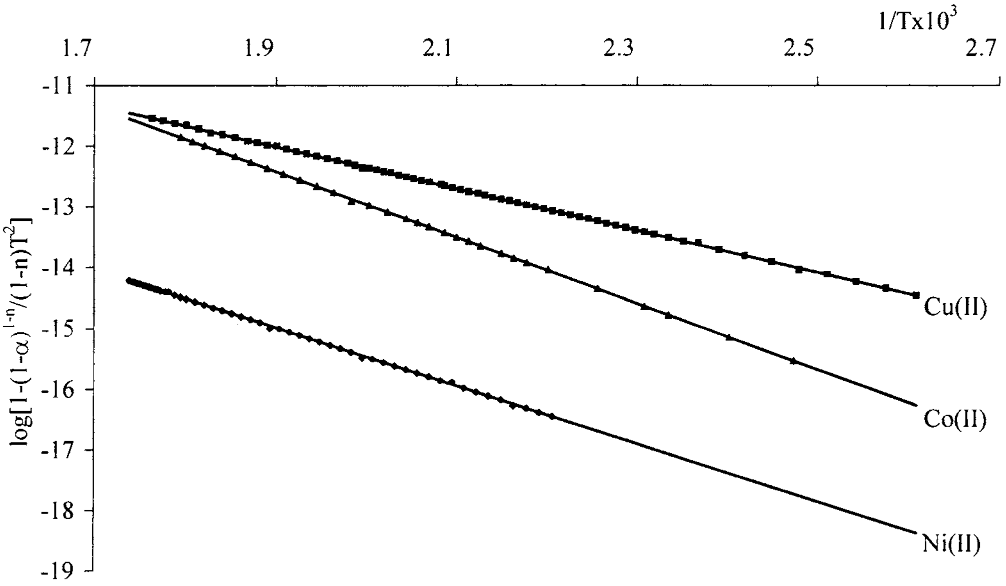

Fig. 7. Linearisation curves of Coats and Redfern method for Co(II)–, Ni(II)–, and Cu(II)-*p*-toluidino-*p*-chlorophenylglyoxime complexes.

Table 2
Kinetic data on the investigated compounds[a]

Sample	Stage	Reaction order (*n*)	Parameters	From Coats and Redfern equation	From Horowitz and Metzger equation
p-T-*p*-CPG	I	1.000	E^*	17.3	17.8
			A	8.6×10^{-2}	12.5×10^{-2}
			ΔS^*	−269.4	−266.3
			r	0.9997	0.9998
	II	1.000	E^*	41.9	42.8
			A	7.7×10^{7}	8.9×10^{7}
			ΔS^*	−72.6	−102.0
			r	0.9932	0.9962
Cu(*p*-T-*p*-CPG)$_2$	I	0.919	E^*	45.5	56.6
			A	236.2	4018.9
			ΔS^*	−203.7	−180.2
			r	0.9994	0.9991
	II	0.916	E^*	36.2	45.0
			A	1.0	5.1
			ΔS^*	−252.1	−238.4
			r	0.9910	0.9945
	III	0.932	E^*	101.9	110.1
			A	571.2	1615.9
			ΔS^*	−202.1	−193.4
			r	0.9991	0.9997
Ni(*p*-T-*p*-CPG)$_2$	I	0.749	E^*	31.2	46.9
			A	0.2	56.6
			ΔS^*	−262.5	−216.7
			r	0.9972	0.9981
	II	0.971	E^*	34.9	37.9
			A	0.6	1.6
			ΔS^*	−255.8	−247.9
			r	0.9896	0.9955
	III	0.990	E^*	96.2	95.1
			A	223.8	247.9
			ΔS^*	−209.8	−208.9
			r	0.9985	0.9995
Co(*p*-T-*p*-CPG)$_2$·2H$_2$O	I	0.847	E^*	45.0	53.5
			A	105.9	823.3
			ΔS^*	−184.8	−193.8
			r	0.9994	0.9986
	II	0.912	E^*	161.3	170.6
			A	1.2×10^{12}	8.0×10^{12}
			ΔS^*	−19.3	−3.7
			r	0.9990	0.9989
	III	0.837	E^*	34.7	45.1
			A	0.1	0.6
			ΔS^*	−271.6	−257.5
			r	0.9985	0.9991

[a] Units of parameters: E^* (kJ mol^{-1}), A (s^{-1}), ΔS^* (mol^{-1} K^{-1}), r: correlation coefficient of the linear plot, n: order of reaction.

1 for each stage of complexes. The kinetic data reached by both of the methods are in harmony with each other.

The values of activation energy E^* obtained by two methods for the ligand and for each of its complexes are given in Table 2. The activation energy of Co(II), Ni(II) and Cu(II) complexes is expected to increase proportional to the decrease in their radius [9]. The activation energy of Ni(II) and Cu(II) complexes which have been decomposed on a similar mechanism and have square-planar structure increase proportional to their radius degrees. E^* values according to the average of two methods for these two complexes in the first decomposition stages are 39.1 and 51.1 kJ mol^{-1}, respectively.

$$E^*_{\mathrm{Cu}} = 51.1\ (r_{\mathrm{Cu}} = 70\,\mathrm{pm}) > E^*_{\mathrm{Ni}} = 39.1\ (r_{\mathrm{Ni}} = 72\,\mathrm{pm})$$

The shorter the radius of metal ion, the easier ligand approaches the central atom. As a result metal–ligand interaction becomes stronger, the detachment of the link becomes more difficult and E^* values increase [10–13]. The same observation is obtained for the second and third decomposition stage of Ni(II) and Cu(II) complexes (see Table 2).

The values of the entropies are negative for all of the compounds. Finally, the negative values of entropies in the decomposition reactions indicate that the reactions are slower than normal [14,15] and also indicate that the activated complexes have more ordered structure than the reactants [13].

The greater the metal–ligand bond energies in the complexes, the smaller the complexed metal ions are. Therefore, decomposition of the complexes to the metal oxides may be initiated by metal–ligand bond breaking, since these complexes decomposed at higher temperatures as $1/r$ is increased (r = radius of metal ion). On the other hand, the oximes of Cu(II) and Ni(II) which decomposes at lower temperatures as $1/r$ increase, may decompose by electron transfer from the oximes to the metal ions. This is supported by the fact that the electron affinities of metal ions, in general increase with increasing effective nuclear charge [16,17].

$$T_{\mathrm{Cu}} = 383\,\mathrm{K}\ (r_{\mathrm{Cu}} = 70\,\mathrm{pm}) < T_{\mathrm{Ni}} = 453\,\mathrm{K}\ (r_{\mathrm{Ni}} = 72\,\mathrm{pm})$$

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