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FACTORS INFLUENCING THE THERMAL DECOMPOSITION OF TRANSITION METAL COMPLEXES WITH 2-OH-ARYLOXIMES UNDER NITROGEN

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The thermal behavior of copper(II), nickel(II) and palladium(II) complexes with two anionic varieties of 2-OH-aryloximes (ox), [M(ox)$_2$] (2-hydroxypropiophenonoxime and 2-hydroxy-4-methoxy-benzophenonoxime) was studied by using simultaneous TG/DTG-DTA technique under nitrogen in the temperature range 40–700°C. The behavior was compared with that in static air, which had been previously studied. It was found that the metal, the substituents on the ligand and the heating rate influenced their thermal decomposition. The thermal stability of the complexes with the same ligand depended on the metallic cation, following the order Pd(II)>Ni(II)>Cu(II). It also depended on the type of ligand, increasing with bulky substituents on the oximic carbon and the benzene ring. The sample mass almost did not affect their decomposition mode. The residues at 700°C of all complexes consisted of a carbonaceous oxide, determined by energy dispersive spectrometry (EDS) and IR spectroscopy

Keywords: *copper complexes, nickel complexes, 2-OH-aryloximes, palladium complexes, thermal properties TG/DTG-DTA, transition metal complexes*

Introduction

The strong coordinating properties of 2-hydroxyaryloximes (ox) with transition metals [1–2] have stimulated researches in finding significant applications in solvent extraction systems and in hydrometallurgy [3–5]. Knowledge of the structural features and the parameters influencing bond formation and chelate stability might help in the design of ligands with predetermined properties. Substituents, aryl or alkyl, attached to the oximic carbon of the hydroxyoximes engender stereoelectronic effects that may influence distinctive physicochemical and biological properties. For instance, Moreley suggested, from theoretical studies, that steric factors were responsible for the different extraction behaviours of various 2-hydroxyaryloximes [6]. Moreover, correlation of the structure of bis(hydroxyaryloximates) with biological activities have been reported [7–8].

In view of these significant applications we have initiated several years ago, a systematic research project on some 3*d*-transition metal complexes with 2-hydroxyaryloximes in order to establish the chemical, electronic and redox properties of the various coordination geometries obtainable within the oxime system [8–12, 16]. The metals Cu, Ni and Pd were selected on the basis of their different electronic configurations and their biological activities. The X-ray studies for some divalent metal (Cu, Ni, Pd) 2-OH-aryloximates, [M(ox)$_2$], reveal a slightly distorted trans square-planar configuration with the M–N bonds being longer than the M–O ones. Strong intramolecular hydrogen bonds between the phenolic oxygen and the hydrogen of the oximic hydroxyl were observed in all the cases [10–11, 13–15].

The thermal behavior of some transition metal complexes of 2-hydroxyaryloximates has received considerable attention [12, 17 and references therein]. Their thermal stability and decomposition mode have been studied in air atmosphere, using the TG-DTA technique, while mass spectrometry (MS) was very helpful for determining the various fragmentation patterns. Recently, there has been an increasing research interest on the thermal properties of transition metal complexes, with ligands having N,O donor abilities like the 2-hydroxyoximes, studied by TG-DTA or TG-MS/DTA techniques [18–19].

Continuing our investigations, the present study involving the thermal behavior of transition metal 2-OH-aryloximates was undertaken in order to explore the factors influencing their thermal decomposition process, such as: *i*) the substituents of the oxime ligands and the structure of the complexes, *ii*) the heating rate, *iii*) the sample mass, and *iv*) the atmosphere around the sample. For this purpose, the

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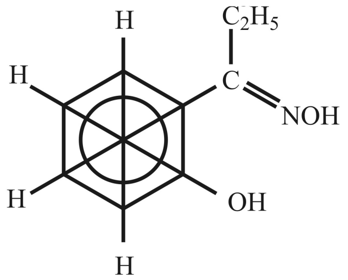
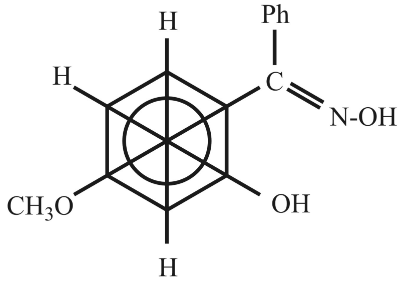


2-hydroxy-propiophenonoxime (Hopox)



2-hydroxy-4-methoxy-benzophenonoxime (Hopox)

Fig. 1 Structural formulas of the two 2-OH-aryloximes used in the present study

TG/DTG-DTA measurements of some complexes of the type [M(ox)$_2$], where M was Cu, Ni and Pd, were recorded in nitrogen atmosphere and in different heating rates. The results are reported and discussed.

Experimental

Materials

Synthesis of the ligands

2-hydroxyaryloximes (ox) were synthesized employing literature methods [20–21]. Figure 1 illustrates the two oximes used in the present work, which are derivatives of 2-hydroxybenzaldoxime (named also salicylaldoxime, Hsaox). They are 2-hydroxyphenyl-1-propanonoxime, known also as 2-hydroxypropiophenonoxime (Hppox) and 2-hydroxyphenyl-4-methoxy-1-benzophenonoxime, known also as 2-hydroxy-4-methoxy-benzophenonoxime (Hopox).

Synthesis of [M(ox)$_2$,], where *M*=Cu(II), Ni(II), Pd(II)

The metal salts (MCl$_2$·*x*H$_2$O, M=Cu, Ni, Pd) were purchased from Fluka in extra pure grade. Samples of bis(2-hydroxyaryloximato) complexes were prepared by the reaction between the metal(II) chloride and oxime in 1:2 metal to ligand ratio as previously reported [9–10].

Methods

The simultaneous TG/DTG-DTA curves for the complexes [M(ox)$_2$] were obtained on a SETARAM instrument, model SETSYS-1200. The samples were heated in platinum crucibles, in nitrogen atmosphere, within the temperature range 40–700°C. The heating rates were 5, 10, 15 and 20°C min^{-1} and the sample size ranged in mass from 10–15 mg. The stoichiometry of the residues was checked by Energy Dispersive Spectrometry (EDS) JSM-840A type analytical system Oxford ISIS-300.

Results and discussion

Six 2-hydroxyaryloxime complexes of the type [M(ox)$_2$] (M(II)=Cu, Ni, Pd) were subjected to simultaneous TG/DTG-DTA analysis from 40 to 700°C in nitrogen atmosphere and at a heating rate 10°C min^{-1}. The temperature ranges, determined percentage mass losses and thermal effects accompanying the decomposition reactions for all the complexes are given in Table 1. Representative examples of thermoanalytical curves at a heating rate of 10°C min^{-1} for complexes with the same ligand and different metals, such as [Cu(opox)$_2$], [Ni(opox)$_2$] and [Pd(opox)$_2$] are presented in Fig. 2.

The main decomposition stage of [M(opox)$_2$] complexes was shown by a sudden mass loss in the TG curves accompanied by a strong exothermic effect in the DTA curves. In the case of palladium this happens after its melting point (shown by an endothermic DTA peak at 304°C), while in the case of copper and nickel the compounds decompose without melting. The profile of the thermoanalytical curves is different for each metal, while their thermal stability, based on the temperature at which the first mass loss stage begins, follows the order Pd>Ni>Cu.

The first decomposition stage was followed by one or two weak endothermic decomposition stages accompanied by further gradual mass loss. The decomposition proceeds with rupture of the coordination bonds by the elimination of one oxime molecule, or with the rupture of bonds inside the ligands, probably by elimination of nitrile, nitriloxide or alcohol molecules as calculated from mass loss on the TG/DTG curves (details for each studied compound are given in Table 1). The kind of evolved molecules was inferred from the Mass Spectral data previously reported for these complexes [17].

As far as the thermal decomposition of the complexes with the same metal and different ligands is concerned, there is a correlation between their thermal stability and the substituents on the ligands. When the substituents were bulky and occur in both,

Table 1 Thermoanalytical features (TG/DTG-DTA) of copper(II), nickel(II) and palladium(II) 2-hydroxyaryloximates under nitrogen

Compound	Stage	Temperature range/°C	DTG_{max}/ °C	DTA Endo/ °C	DTA Exo/ °C	Mass loss/ %	Evolved moiety formula	Mass calc./ %
$[Cu(opox)_2]$	1	240–270	270	–	270	21.0	PhCNO	21.7
	2	270–400	346	348		33.5	$PhCNO+2CH_3O$	33.0
	Residue	>680				30.0	CuO+C	14.5+*x*
$[Cu(ppox)_2]$	1	200–300	222, 248	179	222, 248	41.0	HL	42.1
	2	300–680	397, 582	397, 582		19.4	EtOH+HCN	18.6
	Residue	>680				35.0	CuO+C	20.3+*x*
$[Ni(opox)_2]$	1	250–300	278	–	278	17.0	PhOH	17.3
	2	300–470	401	401		33.0	$PhCNO+2CH_3O$	33.3
	3	470–680	550	550		19.5	PhCN	18.9
	Residue	>680				25.0	NiO+C	13.8+*x*
$[Ni(ppox)_2]$	1	220–270	239	190, 200	239	10.0	HCNO	10.8
	2	270–320	302		302	13.5	EtCN	14.2
	3	320–500	388	388		24.5	PhOH	24.3
	Residue	>680				25.0	NiO+C	19.4+*x*
$[Pd(opox)_2]$	1	305–340	332	304	332	40.0	HL	41.0
	2	340–400	348	348		20.0	PhCNO	20.1
	Residue	>680				40.0	PdO+C	20.7+*x*
$[Pd(ppox)_2]$	1	235–400	341	204	341	52.6	HL+EtCNO	54.3
	Residue	>680				45.0	PdO+C	28.2+*x*

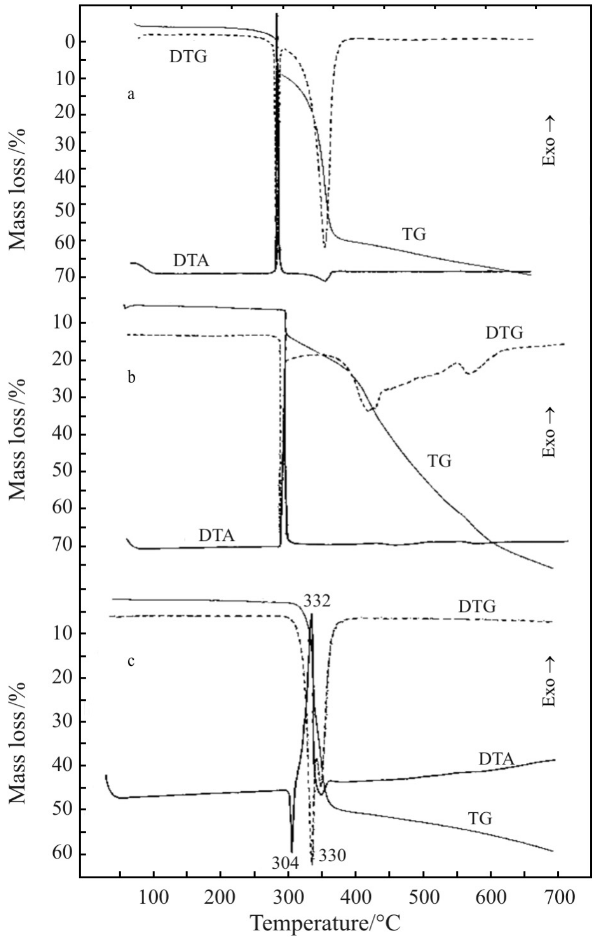


Fig. 2 Thermoanalytical curves of a – [Cu(opox)$_2$], b – [Ni(opox)$_2$] and c – [Pd(opox)$_2$] recorded under nitrogen, at a heating rate of 10°C min^{-1}

the oximic carbon and the benzene ring, as in the case of opox, with a phenyl group attached to the oximic carbon and a methoxy group attached to the benzene ring, the thermal stability of the complex is greater compared with the analogous complex of the ppox ligand, where there is a small ethyl group attached to the oximic carbon and no methoxy group attached to the benzene ring.

The intermediates formed after the first decomposition stage, which was the main degradation step, were not stable and upon further heating the residues of all the complexes at 700°C they were composed of a carbonaceous metal oxide, as it was inferred from energy dispersive spectrometry (EDS) and IR data.

In order to determine the effect of heating rate on the decomposition process of the studied compounds [M(ox)$_2$], the following complexes [Cu(opox)$_2$], Ni(ppox)$_2$] and Pd(ppox)$_2$] were chosen and subjected for thermal measurements at different heating rates (5, 10, 15 and 20°C min^{-1}) with the same mass sample. From the thermoanalytical data of [Cu(opox)$_2$] complex at different heating rates, it was deduced that the residue CuO at 700°C had smaller amount of carbon at low heating rates (5 or 10°C min^{-1}), than at higher (15 or 20°C min^{-1}). Evidence for this observation came from the estimated total mass loss on the TG curves of the complexes and verified from the Energy Dispersive Spectrometry (EDS) data of their residues. That means that, under nitrogen atmosphere, the decomposition of oximates was incomplete and that there was a relation between the heating rate and the extent of decomposition. The position of the exothermic peak on DTA

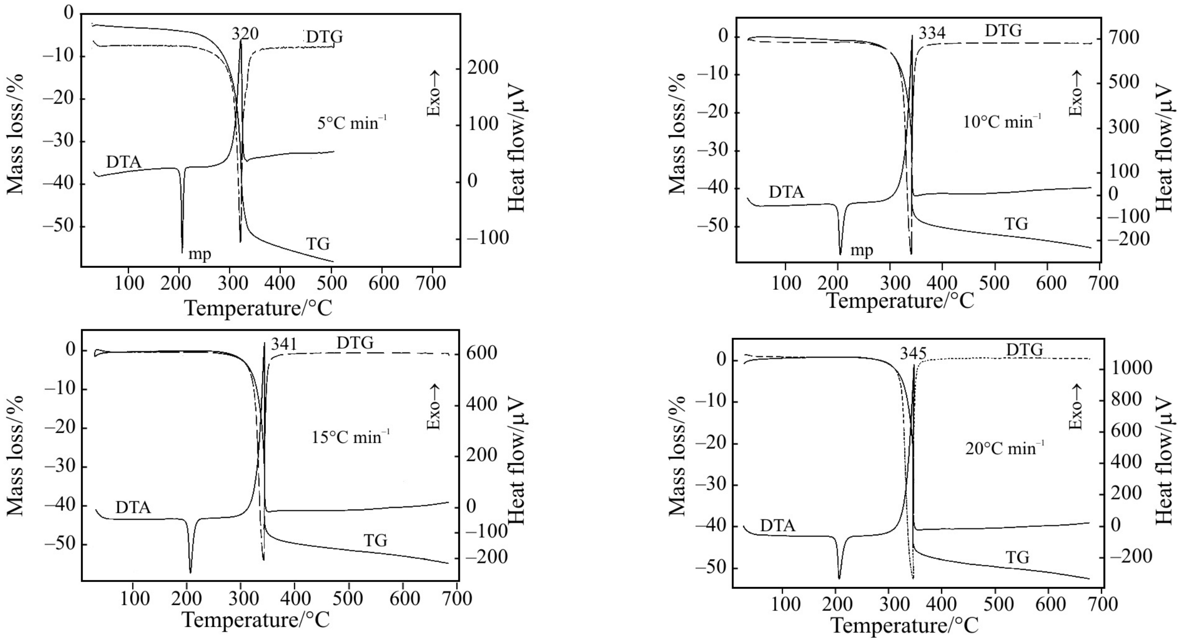


Fig. 3 Thermoanalytical curves of [Pd(ppox)$_2$] at different heating rates recorded under nitrogen

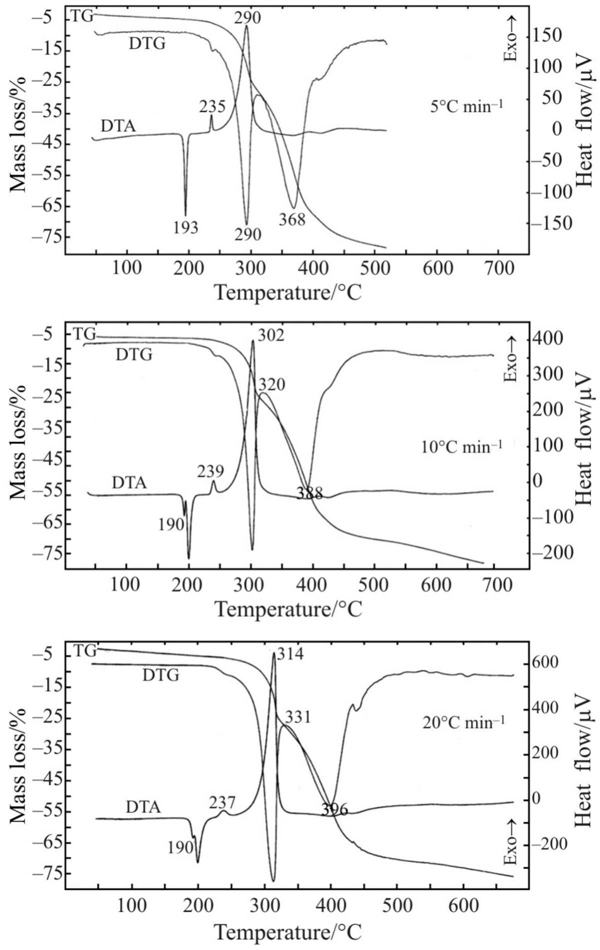


Fig. 4 Thermoanalytical curves of [Ni(ppox)$_2$] at different heating rates recorded under nitrogen

curves was observed at higher temperatures with increasing heating rate, as it was expected.

The same results were obtained for the complex [Pd(ppox)$_2$] when the TG/DTG-DTA curves were recorded at four different heating rates, as is illustrated in Fig. 3. It is worthwhile to mention, however, that the temperature of the melting point did not alter dramatically with the heating rate, whereas the decomposition was observed at higher temperatures.

In order to determine the influence of mass size on the thermal decomposition mode of the palladium oximates, the thermoanalytical curves of the complex [Pd(ppox)$_2$] were recorded with three different mass 10, 15 and 20 mg. The results showed that there was no influence of the sample size on the final residue, as well as on the melting point temperature, but there was a small effect on the decomposition temperature, which became higher with increasing sample mass. This effect is best observed in the case of [Ni(ppox)$_2$] complex (Fig. 4).

The melting point of [Ni(ppox)$_2$] complex, determined on a Reichert heated plate apparatus was found to be 189–190°C [10], and on the DTA curve, recorded at 5°C min^{-1} under nitrogen atmosphere, was observed at 193°C. However, when the heating rate for the same complex was 10 or 20°C min^{-1}, two endothermic peaks instead of one were observed at 190 and 200°C. It was also observed that the temperature of the exothermic peak for the main decomposition stage at 290°C at a heating rate of 5°C min^{-1}, shifted to 314°C at a heating rate of 20°C min^{-1}. This phenomenon may be explained if we take into consideration the high degree of crystallinity of this compound and the shape of the endothermic peaks of the DTA curves. The compound crystallizes in the monoclinic crystal system, containing in the unit cell two Ni(ppox)$_2$ units with strong hydrogen bonds [10]. At small heating rates, the compound has the sufficient time to absorb heat and to transfer from the solid to the liquid phase by loosening some bonds in the crystal lattice. At higher heating rates, this process cannot be completed at the same time but the recorded temperature rises, resulting in the appearance of two endotherms instead of one, the second being at a higher temperature. Another possible explanation would be that with high heating rate the original sample is transformed first to a meta-stable solid phase, which melts only at elevated temperatures.

The influence of the atmosphere on the thermal decomposition of the studied complexes is very significant leading to different final products as it was expected, due to the oxidation process that takes place in air atmosphere. So, in air atmosphere, pure metal oxides are formed at ~500°C [17], in accordance with other similar results on salicylate and cefadroxil transition metal complexes [22–23], while in nitrogen the residues at 700°C consist of carbonaceous metal oxides.

From X-ray studies, it is well known that in the complexes under investigation there are strong intramolecular bonds between the phenolic oxygen and the hydrogen of the oximic hydroxyl. The hydrogen bond distances (O–O’) of Ni(ppox)$_2$ [10], Cu(ppox)$_2$ [13] and Pd(ppox)$_2$ [11], which are 248, 258 and 259 pm respectively, are in agreement with the negative shift of the oximic hydroxyl group (510, 385 and 380 cm^{-1} respectively) that was observed in the IR spectra of these complexes [9–10].

The activation energies, calculated from the TG data for the first decomposition stage in air atmosphere of the nickel, palladium and copper propiophenoxime (ppox) complexes, were found to be 274, 215 and 196 kJ mol^{-1}, respectively [17]. Considering the X-ray, spectroscopic (IR) and thermal (TG/DTG-DTA) results of the investigated ppox complexes, it was concluded that their thermal stability in air, which depends on the activation energies, is correlated with the strong hydrogen bonds of the complexes. From the present results it seems that there is a correlation between the activation energies for the first decomposition stage, although determined previously in air atmosphere, and the first decomposition exothermic DTA peaks of the different ppox complexes, as determined under nitrogen in the present study.

Conclusions

The DTA and TG/DTG curves of the 2-OH-aryloxime complexes with Cu, Ni and Pd recorded under nitrogen, show that these substances possess a sharp intense exothermic decomposition followed by one or two very weak endothermic decompositions accompanied by mass loss. The decomposition mode depends on the metal and the substituents of the ligand involved.

The thermal stability under nitrogen, based on the initial decomposition temperature for the complexes with the same ligand follows the series Pd>Ni>Cu, while for the complexes with the same metal it becomes greater with bulky substituents in both the oximic carbon and the benzene ring of the ligand.

In air atmosphere, pure metal oxides are formed at ~500°C, while under nitrogen the residues at ~700°C for all the complexes consist from a carbonaceous oxide.

The thermal stability, based on the estimated activation energies for the first decomposition stage in air, is correlated with the existed strong intramolecular hydrogen bonds of the complexes.

Different heating rates resulted in different decomposition temperatures and in different amounts of carbon contents in the metal oxide residue.

The sample size has no great influence on the thermal decomposition of the studied complexes.

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