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MECHANISM OF THERMAL DEHYDROCHLORINATION
o-Hydroxyacetophenone Girard-P hydrazone transition metal cation chloride complexes

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Abstract

Co(II), Ni(II), Cu(II) and Zn(II) complexes of *o*-hydroxyacetophenone Girard-P hydrazone were prepared by using the organic ligand and the corresponding transition metal chlorides. The protonation and formation constants were evaluated for the organic ligand *o*-hydroxyacetophenone Girard-P hydrazone and its transition metal complexes, respectively. The thermal behaviour of the test materials was established by means of DTA. Their semiconducting parameters were evaluated through DC-conductivity measurements, and their thermodynamic parameters were evaluated, assigned and interpreted. The mechanism of thermal dehydrochlorination of the metal chloride complexes was proposed.

Keywords: complexes, dehydrochlorination, DTA

Introduction

Many of the physiologically active hydrazones find application in the treatment of diseases such as tuberculosis, leprosy and mental disorders [1, 2]. Hydrazones also act as herbicides, insecticides, nematocides, rodenticides and plant growth regulators. In analytical chemistry, the formation of hydrazones is extensively used in the detection, determination and isolation of compounds containing carbonyl groups.

The kinetic parameters of the thermal decompositions of the Zn, Cd and Hg hydrazones of anisaldehyde Girard-T were determined from the corresponding thermal curves [3]. The orders of the reactions and the activation energies were determined.

The present work was carried out as a continuation of our previous investigations on hydrazone derivatives with transition metals [1, 4 and 5] and on the electrical conductivity and thermal studies of different hydrazones [6].

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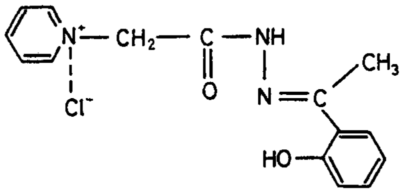
The present investigation reports an extensive study of the protonation and formation constants, thermal behaviour and semiconductivity of *o*-hydroxyacetophenone Girard-P hydrazone and its Co(II), Ni(II), Cu(II) and Zn(II) complexes, in an attempt to evaluate their thermal and electrical activation energies, the reaction order and the mechanism of their thermal changes.

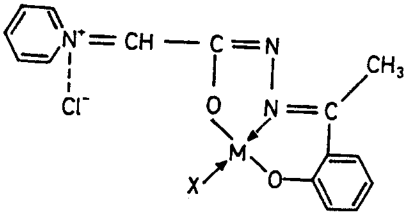
Experimental

Preparation of metal complexes

Solutions of metal chlorides were prepared, using double distilled water, from analytical grade salts. All solutions were standardized by established procedures [7]. The ligand *o*-hydroxyacetophenone Girard-P hydrazone (H_2L) and its Co(II), Ni(II), Cu(II) and Zn(II) complexes were prepared and their molecular structures were determined as follows:



The organic ligand (H_2L)



The transition metal complexes $X = H_2O$, M = Co, Ni, Cu or Zn

Determination of formation constants

For determination of the formation constants, an Extech 671 digital *pH*-meter was used for *pH* measurements; to avoid errors arising from the solvent and the ionic strength of the medium, the *pH*-meter readings were converted to hydrogen ion concentrations by the Van Uitert and Hass method [8]:

$$-\log[H^+] = B + \log U_H \tag{1}$$

where B is the *pH*-meter reading in the ethanol-water mixture, and $\log U_H$ is the correction factor for the *pH*-meter reading. For this purpose, readings were made on a series of 50% aqueous ethanol solutions containing known amounts of HCl and KCl such that the ionic strength (I) was 0.1 M at 25±0.1°C. The value of $\log U_H$ was evaluated to be −0.88. The formation constants were determined by using the following mixtures:

i) 2.5 ml of 2 *M* KCl +1 ml of 0.1 *M* HCl,
ii) mixture (i) +5 ml of 0.1 *M* ligand solution,
iii) mixture (ii) +1 ml of 0.2 *M* metal chloride solution.

The total volume of each mixture was made up to 50 ml containing 50% ethanol and KCl (ionic strength 0.1 *M*). The mixtures were separately titrated with carbonate-free 0.481 *M* KOH solution. From the *pH* titration curves, the values of n_H, n and p^L were calculated as reported previously [9].

Differential thermal analysis (DTA)

DTA was carried out with a Shimadzu DT-30 Thermal Analyzer (Shimadzu, Koyoto, Japan) from room temperature up to ≅500°C under ambient atmosphere.

Electrical conductivity measurements

The DC-electrical conductivity was measured by means of the two-probe method in the temperature range between room temperature and 500 K.

Results and discussion

The protonation constant ($\bar{n}$) of *o*-hydroxyacetophenone Girard-P hydrazone was calculated from the potentiometric titration curves of HCl in the presence and absence of the ligand by the Nayan and Dey method [10]:

$$\bar{n} = [(v' - v'')(N^0 + E^0)]/(v^0 + v')T^0_{C_L}] \tag{2}$$

where v' and v'' are the volumes of alkali required to reach the same *pH* in the titration of mixtures (i) and (ii), respectively, v^0 is the initial volume of the titrated solution, N^0 is the normality of the alkali, E^0 is the initial concentration of the free acid and $T^0_{c_L}$ is the total ligand concentration.

The formation curve extended between 0 and 2 on the n_H scale and from $pH=5$ to $pH=11$; it indicated that the ligand has two dissociable protons. The values of the protonation constants $\log k_2=7.7$ and $\log k_1=10.7$ were taken directly from the formation curve (Fig. 1).

The titration curves of the metal complexes and the organic ligand are well separated, indicating the liberation of protons during the complexation process.

The values of $\bar{n}$ and p^L were also evaluated by the Nayan and Dey method [10]:

$$\bar{n} = [(v' - v'')(N^0 + E^0)]/[(v^0 + v')T^0_{C_M}\,\bar{n}_H] \tag{3}$$

and

$$p^L = \log[k_1k_2[H^+][H^+]^2(v^0 + v''') \,/\, [T^o_{C_L} - \bar{n}T^o_{C_M}v^0] \tag{4}$$

where v', v'' and v''' denote the volumes of alkali required to reach the same pH value in the titration of mixtures (i), (ii) and (iii), respectively, v^0 is the initial volume of the titrated solution, N^0 is the normality of the alkali, E^0 is the initial concentration of the free acid, $T_{C_M}^0$ is the total metal ion concentration, and k_1 and k_2 are the ligand proton dissociation constants. The graph of $\bar{n}$ *vs.* p^L was plotted, as shown in Fig. 1.

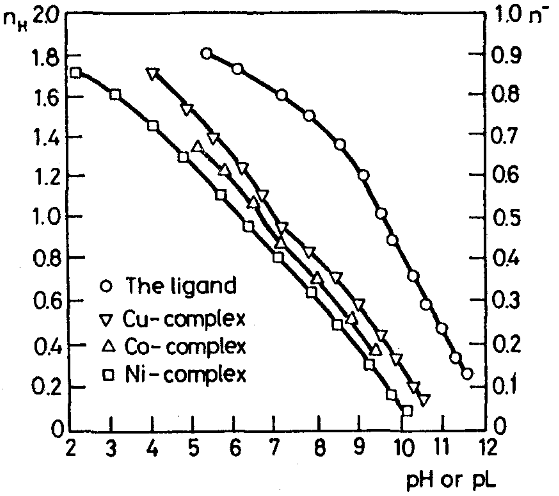


Fig. 1 The formation curves n_H or $\bar{n}$ *vs.* pH or p^L of the ligand and metal – ligand complexes in 50% ethanol (H_2O, I=0.1 M KCl at 25°C)

The formation curves of the metal – ligand complexes for Co(II), Ni(II), Cu(II) and Zn(II) show that the n values attain a maximum value of unity, thus indicating that in solution only one complex, ML, is formed. The evaluated values of $\log k_1$ are 6.60, 6.10 and 7.00 for the complexes of Co(II), Ni(II) and Cu(II), respectively.

Figure 2 shows the DTA curves of the organic ligand and its Co(II), Ni(II), Cu(II) and Zn(II) complexes. Table 1 lists the evaluated thermodynamic and kinetic data, together with their assignments for *o*-hydroxyacetophenone Girard-P hydrazone and its transition metal complexes. The DTA curves for these materials are given in Fig. 2.

The DTA curves (Fig. 2) for the organic ligand display a weak, broad peak at 60°C, due to the removal of physisorbed water from the ligand; a strong, sharp endothermic peak at 260°C, assigned to its melting; and a small, sharp exothermic peak at 300°C, which might be assigned to the thermal dehydrochlorination (HCL loss) of the organic ligand.

For the Co(II) complex, the DTA curve displays an endothermic trough at 228°C, assigned to the loss of coordinated water; dehydrochlorination; an exothermic shoulder at 395°C, due to oxidative thermal decomposition of the complex; and a medium exothermic hump at 490°C, which is assigned to the phase change due to the formation of higher cobalt oxides [11].

Table 1 Thermodynamic and kinetic data together with their assignments for the organic ligand and its transition metal (T.M.) complexes

Material	T/°C (Type of thermal change)	E_a/ kJ mol^{-1}	Reaction order n	Peak characterization
Ligand	60 (endo)	175.6	0.92	dehydration of humidity water content of the ligand
	260 (endo)	359.0	1.26	melting of the organic ligand
	300 (exo)	–	–	thermal HCl loss
Co(II) complex	228 (endo)	121.2	1.18	dehydration of the coordination water (x) molecule
	385 (exo)(vs)	124.9	1.31	thermal dehydrochlorination (HCl loss)
	395	–	–	thermal decomposition of the complex
	490 (exo)	–	–	phase change due to the formation of higher cobalt oxides
Ni(II) complex	100 (endo)	82.1	1.37	dehydration of humidity water
	200 (endo)	116.2	1.43	loss of the coordinated water (x)
	480 (exo)	–	–	HCl loss
	490 (exo)	–	–	thermal decomposition of the complex
Cu(II) complex	278 (exo)	224.0	0.98	oxidative degradation of the complex together with loss of coordinated water (x)
	450 (exo)	–	–	thermal HCl loss
	468 (exo)	–	–	thermal decomposition of the complex
Zn(II) complex	310 (endo)	–	–	thermal loss of the coordinated water molecule (x)
	330 (exo)	121.2	1.7	thermal HCl loss together with thermal decomposition of the complex

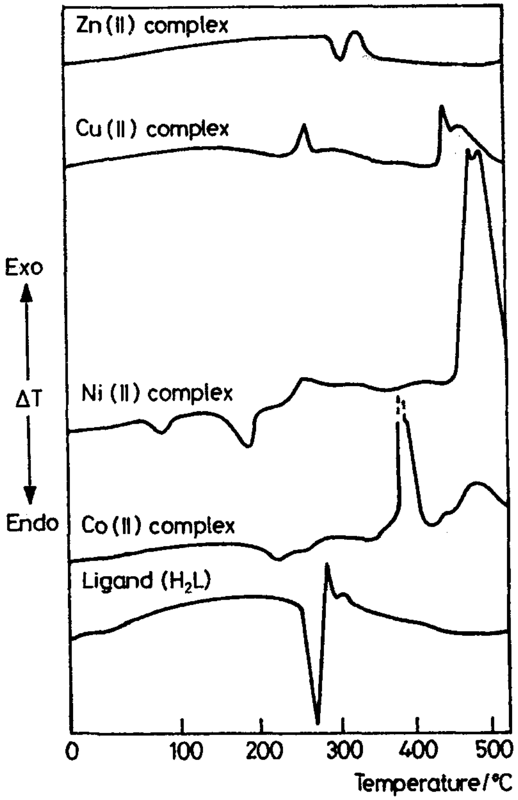


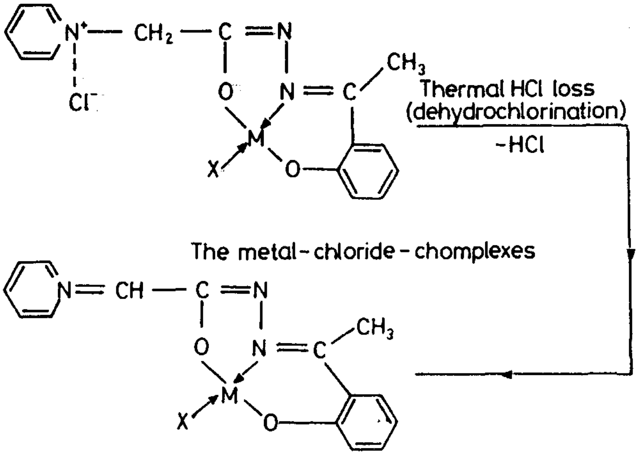
Fig. 2 The DTA curves of the organic ligand (H_2L) and its transition metal complexes

For the Ni(II) complex, the DTA curve displays a small, broad endothermic peak at 100°C, due to loss of the physically absorbed water; a medium endothermic trough at 200°C, assigned to loss of the coordinated water molecules from the core of the complex; a strong, sharp exothermic peak at 480°C, due to dehydrochlorination of the complex; and a strong, broad exothermic peak at 490°C, due to oxidative thermal decomposition of the complex [12].

For the Cu(II) complex, the DTA curve contains a small stepwise exotherm at 235°C, assigned to oxidative degradation of the complex through partial rupture of the chelate bond, together with loss of the coordinated water molecules; a medium, sharp exotherm at 450°C, due to dehydrochlorination of the complex; and a medium, broad exotherm at 480°C as a result of oxidative thermal decomposition of the complex [11].

For the Zn(II) complex, the DTA spectrum exhibits a broad endotherm at 310°C, due to loss of the water from the inner sphere of the complex; and a sharp exotherm at 330°C, assigned to thermal oxidative decomposition of the complex.

Since these transition metal chloride complexes undergo stabilization through dehydrochlorination, the mechanism of thermal HCl loss is exothermic and runs as follows:



The stable illide structure of the complexes; $X = H_2O$, M = Co, Ni, Cu or Zn

This may result in the formation of stable illide complexes, which are thermally decomposed at higher temperatures.

The thermal activation energies (E_a, kJ mol^{-1}) were calculated from the DTA curves (Fig. 2) by the method of Piloyan *et al.* [13]. The E_a values are given in Table 1.

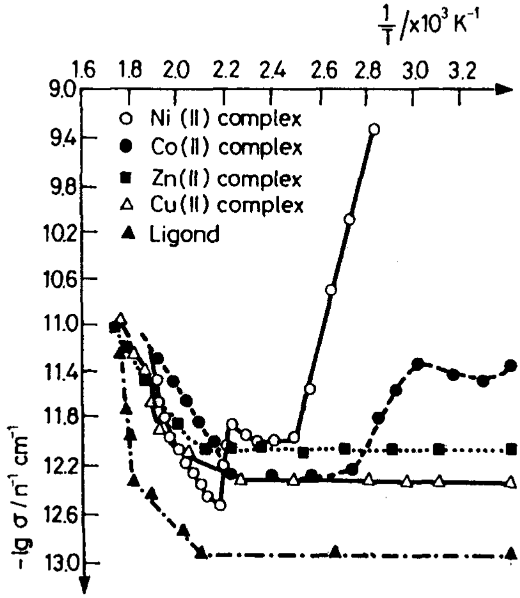


Fig. 3 The variation of electrical conductivity (logσ) *vs.* temperature (1000/T K^{-1}) for the organic ligand (H_2L) and its transition metal complexes

The order of the thermal reaction (n) was determined from the changes observed in the DTA curves as the heating rate was changed, i.e. from the symmetry of the DTA curve, by using the Reich [14] empirical relation of the following form:

$$\text{reaction rate } (\bar{n}) = 1.26\sqrt{\frac{a}{b}} \tag{6}$$

where a/b is the peak shape factor (symmetry of the peak). The data are given in Table 1.

Figure 3 shows the logarithmic electrical conductivity (σ) *vs.* the reciprocal of absolute temperature ($1000/T$, K^{-1}) for the organic ligand and its metal complexes.

It can readily be seen that in the temperature range >180°C the relation is a straight line, displaying a positive temperature coefficient of electrical conductivity for the organic ligand and its metal complexes.

The DTA curves reveal a phase change at ≅260°C for the Co(II) complex and at ≈200°C for the Ni(II) complex, with an abrupt change in the $\log\sigma$ *vs.* temperature relation (Figs 2 and 4).

The Co(II) and Ni(II) complexes display a positive temperature coefficient of electrical conductivity (PTρ) in the relatively low temperature region (Fig. 3). This behaviour might be attributed to the loss of coordinated and/or humidity water [15] from the complex, as indicated in Table 1.

Values of the energy gap (E_g, eV) for the organic ligand and the complexes were calculated via plots of the Arrhenius equation of the type

$$\sigma = \sigma_0 e^{-E_g/2kT} \tag{7}$$

where σ is the electric conductivity at temperature T, σ_0 is the pre-exponential constant, E_g is the energy gap (eV), k is the Boltzmann constant and T is the absolute temperature for each reading. The energy gap (intrinsic activation energy, E_g) data were evaluated and are compiled in Table 2 for the organic ligand and its metal complexes. From Table 2, it can readily be deduced that, on passing from the organic ligand to the transition metal complexes, the energy gap becomes lower and the conductivity higher. This might be ascribed to the transition metal ion acting as a bridge, facilitating the current flow between the organic ligand molecules in the parent complex.

Table 2 The calculated energy gap (E_g/eV)

Material	ΔE / eV
Organic ligand	5.3
Co(II) complex	1.2
Ni(II) complex	1.3
Cu(II) complex	1.15
Zn(II) complex	1.1

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