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THERMAL STABILITY OF SOME AZO-DERIVATIVES AND THEIR COMPLEXES

1-(2-benzothiazolyl)-3-methyl-4-azo-pyrazil-5-one derivatives and their Cu(II) complexes

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Abstract

This paper deals with the first investigation concerning the thermal stability of two 1-(2-benzothiazolyl)-3-methyl-4-azo-pyrazil-5-one derivatives and their Cu(II) coordination compounds of type $((C_4H_9)_4N)_2[Cu(L)_2]$. The thermal decomposition steps were established.

Keywords: azo-derivative, Cu(II) complex, thermal stability

Introduction

The thermal decomposition of the complexes is used to obtain information about their properties as well as about the nature of intermediate and final products. In our previous papers the results concerning the thermal stability and non-isothermal decomposition kinetics of many coordination compounds were presented [1–9].

Azo-derivatives are very important pigments for the synthetic leather and vinyl polymers. Therefore their thermal stability is very important for practical applications. In the last years there were published some papers concerning the study of some organic compounds and their complexes [10–13].

Recently, a new series of 1-(2-benzothiazolyl)-3-methyl-4-azo-pyrazil-5-one derivatives and their Cu(II) complexes were prepared [14].

The major goal of this paper was the study of the thermal behaviour of two azo-derivatives and their Cu(II) complexes in order to throw more light on the solid–gas reactions of these compounds.

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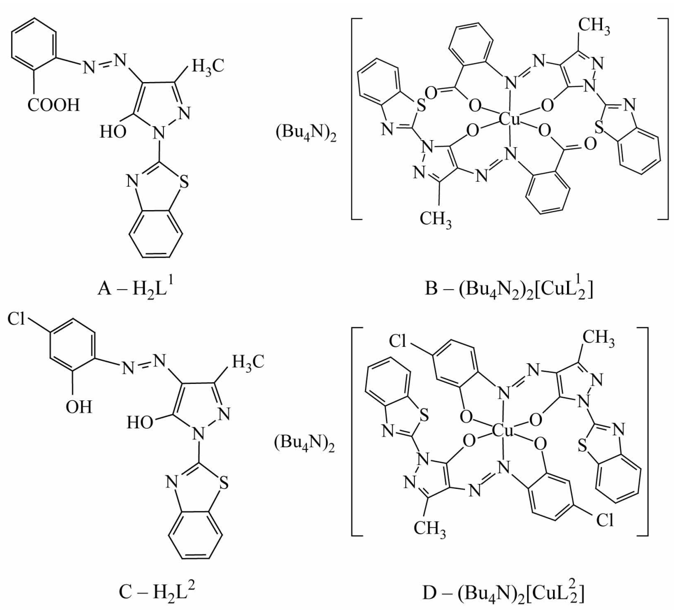


A – H_2L^1 B – $(Bu_4N_2)_2[CuL^1_2]$

C – H_2L^2 D – $(Bu_4N)_2[CuL^2_2]$

Compounds (A)–(D)

Experimental

The compounds (A)–(D) have been synthesised and characterised by chemical analysis, electronic, IR and RPE spectra [14]. All complexes have been synthesized by dissolving 10 mmoles of ligand in 50 mL EtOH at pH=7.5 (adjusted from 4.5 in the free ligand to the 7.5 value with an aqueous solution of tetra-*n*-butylammonium hydroxide 3%). This solution has been stirred at room temperature and an aqueous solution of 50 mmoles $Cu(CH_3COO)_2 \cdot H_2O$ was added drop wise to wise. The mixture of the reaction was stirred for 0.5 h and the brown solid complexes were filtered off, recrystallised from EtOH and dried at room temperature.

The thermal decomposition curves have been recorded by a derivatograph (MOM Budapest) in the temperature range of 20–1000°C. Heating rates were in the range of 2.8–10 K min^{-1}.

The chemical analysis and IR spectral data were used to confirm the nature of the intermediates and also the final products.

IR spectra were recorded in KBr pellets with a FTIR-BIORAD instrument.

Results and discussion

The following solid compounds have been used:

$$H_2L^1 \text{ or } C_{18}H_{13}N_5O_3S \qquad (A)$$

$$((C_4H_9)_4N)_2\ [CuL^1_2]\ \text{or}\ CuC_{68}H_{94}N_{12}O_6S_2 \qquad \text{(B)}$$

$$H_2L^2\ \text{or}\ C_{17}H_{12}ClN_5O_2S \qquad \text{(C)}$$

$$((C_4H_9)_4N)_2[CuL^2_2]\ \text{or}\ CuC_{66}H_{92}Cl_2N_{12}O_4S_2 \qquad \text{(D)}$$

Table 1 Thermoanalytical data of the compounds (A) and (B) (the mass loss, Δ*m*, was calculated related to the corresponding residue)

Compound	Step	Thermal effect	*T*/ °C	Δm_{exp}/ %	Δm_{calc}/ %
$C_{18}H_{13}N_5O_3S$ (A)	A.1	exo	160–320	32.36	32.18
	A.2	exo	420–590	67.64	67.72
$[(C_4H_9)_4N]_2[Cu(C_{18}H_{11}N_5O_3S)_2]$ (B)	B.1	exo	260–315	38.02	37.03
	B.2	exo	370–520	51.21	52.13
	B.3	exo	680–760	3.76	3.99
		Res. CuCN		7.01	6.87

Table 2 Thermoanalytical data of the compounds (C) and (D) (the mass loss, Δ*m*, was calculated related to the corresponding residue)

Compound	Step	Thermal effect	*T*/ °C	Δm_{exp}/ %	Δm_{calc}/ %
$C_{17}H_{12}ClN_5O_2S$ (C)	C.1	exo	180–335	33.82	33.33
	C.2	exo	400–615	66.11	66.67
$[(C_4H_9)_4N]_2[Cu(C_{17}H_{10}ClN_5O_2S)_2]$ (D)	D.1	exo	155–335	37.24	36.66
	D.2	exo	440–725	55.92	56.52
		Res. CuCN		6.84	6.81

Both the results concerning the thermal decomposition/degradation of the organic ligands and their Cu(II) complexes are comparatively presented in the following. Tables 1 and 2 summarise the thermogravimetric data.

Thermal decomposition of $C_{18}H_{13}N_5O_3S$ (A)

According to the TG curve at progressive heating (Fig. 1), the following decomposition steps have been evidenced:

$$C_{18}H_{13}N_5O_3S_{(s)}\rightarrow C_{11}H_7N_5OS_{(l)}+C_7H_6O_{2\,(g)} \qquad \text{(A.1)}$$

$$2C_{11}H_7N_5OS_{(l)}+73/2O_{2\,(g)}\rightarrow 22CO_{2\,(g)}+7H_2O_{(g)}+10NO_{2\,(g)}+2SO_{2\,(g)} \qquad \text{(A.2)}$$

The first decomposition step occurred in the temperature range 160–320°C with a weak exothermic effect. This step corresponds to the C_{arom}–N bond cleavage, leading to the gaseous benzoic acid formation (the benzoic acid can be eliminated as it is

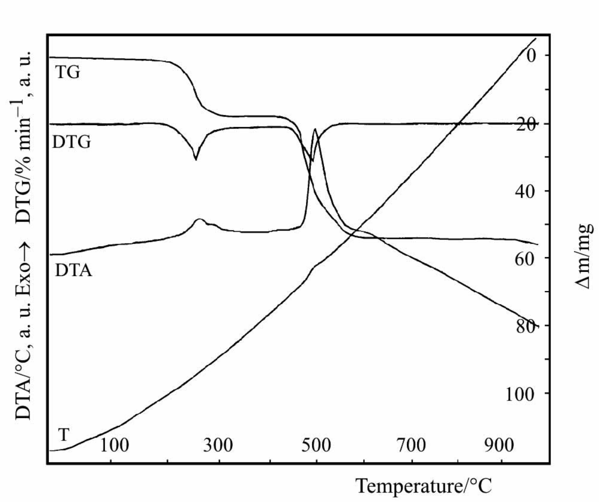
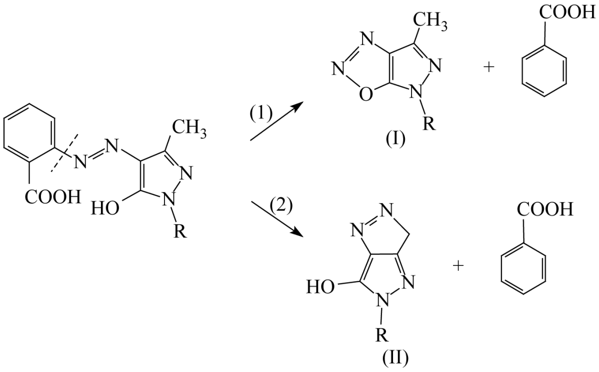


Fig. 1 TG, T, DTG and DTA curves of organic compounds HL^1 (sample mass: 54 mg)

or its oxidative degradation may occur, its boiling temperature is 249.2°C [15]). The rest of the organic component suffers a cyclisation reaction by forming either a new oxodiazole (I) or diazole (II) ring as it is shown in Scheme 1.



Scheme 1

The chemical elemental analysis was used in order to confirm the composition of the solid residue (found: C, 51.25; N, 27.31; H, 2.80; S, 12.35%; requires for $C_{11}H_7N_5OS$: C, 51.36; N, 27.23; H, 2.72; S, 12.45%).

The absence of the band corresponding to the stretching vibration ν(OH) from the IR spectrum of the reaction product represents a proof of the compound (I) formation [16].

The second decomposition step is accompanied by a strong exothermal effect and it corresponds to the oxidative degradation of the previous compound (I).

Thermal decomposition of $[(C_4H_9)_4N]_2[Cu(C_{18}H_{11}N_5O_3S)_2]$ (B)

The TG and DTG curves (Fig. 2) indicate that the thermal decomposition occurs through the following steps:

$$[(C_4H_9)_4N]_2[Cu(C_{18}H_{11}N_5O_3S)_2]_{(s)}\rightarrow$$

$$[Cu(C_7H_5O_2)_2(C_{11}H_7N_5OS)_2]_{(s)}+2(C_4H_9)_3N_{(g)}+2C_4H_{8\,(g)} \qquad (B.1)$$

$$x[Cu(C_7H_5O_2)_2(C_{11}H_7N_5OS)_2]_{(s)}+39xO_{2\,(g)}\rightarrow$$

$$x\text{CuCN}_{(l)}+2(\text{CN})_{2x\,(s)}+31xCO_{2\,(g)}+12xH_2O_{(g)}+3xNO_{2\,(g)}+2xSO_{2\,(g)} \qquad (B.2)$$

$$x\text{CuCN}_{(l)}+2(\text{CN})_{3x\,(s)}+12xO_{2\,(g)}\rightarrow x\text{CuCN}_{(l)}+6xCO_{2\,(g)}+6xNO_{2\,(g)} \qquad (B.3)$$

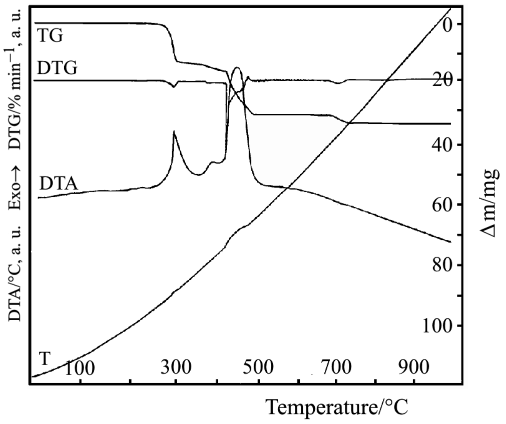


Fig. 2 TG, T, DTG and DTA curves of $[(C_4H_9)_4N]_2[CuL^1_2]$ (sample mass: 36 mg)

The thermal decomposition of this complex occurs similar with that of the organic ligand, excepting the fact that, although the first step occurs with the cleavage of C–N bond, the benzoate ion which resulted still remains coordinated to the metal ion. This step occurs at the same time with the thermal decomposition of tetrabutylammonium ion in tributylamine and butane [15].

Next step, which is accompanied by a strong exothermic effect, corresponds to the oxidative degradation of the organic component and to the reduction of complex copper ion to copper cyanide, which is very stable (*m.p.* 473°C; *b.p.* >1300°C) [17]. The nature of this residue was confirmed by the chemical elemental analysis (found: Cu, 37.75; C, 28.31; N, 33.56%; requires for CuCN + $(CN)_3$: Cu, 37.91; C, 28.65; N, 33.43%). and the IR spectrum (which exhibits the characteristic vibration band ν(CN) at about 2100 cm^{-1}).

The solid residue obtained after this step, which according to literature data [18] is the paracyanide, undergoes further depolymerisation. The dicyanide which results in this process suffers then an oxidative degradation at temperatures higher than

800°C. The final reaction product, CuCN, was confirmed by the chemical elemental analysis (found: Cu, 70.81; C, 13.30; N, 15.75%; requires for CuCN: Cu, 70.95; C, 13.41; N, 15.64%).

Thermal decomposition of $C_{17}H_{12}ClN_5O_2S$ (C)

According to the heating curves, the thermal decomposition occurs in two steps.

$$C_{17}H_{12}ClN_5O_2S_{(s)} \rightarrow C_{11}H_7N_5OS_{(l)} + C_6H_5ClO_{(g)} \qquad (C.1)$$

$$2C_{11}H_7N_5OS_{(l)} + 73/2O_{2\,(g)} \rightarrow 22CO_{2\,(g)} + 7H_2O_{(g)} + 10NO_{2\,(g)} + 2SO_{2\,(g)} \qquad (C.2)$$

The first exothermic step corresponds to a complex process in which occurs the cleavage of C–N bond, the formation of oxodiazole ring and also the volatilisation of 2-chlorophenol (*b.p.* 175–176°C).

Next step, which is accompanied by a strong exothermic effect, corresponds to the oxidative degradation of the compound resulted in reaction (C.1).

Thermal decomposition of $[(C_4H_9)_4N]_2[Cu(C_{17}H_{10}ClN_5O_2S)_2]$ (D)

The heating curves exhibit the following thermal decomposition steps:

$$[(C_4H_9)_4N]_2[Cu(C_{17}H_{10}ClN_5O_2S)_2]_{(s)} \rightarrow$$
$$[Cu(C_6H_4ClO)_2(C_{11}H_7N_5OS)_2]_{(s)} + 2(C_4H_9)_3N_{(g)} + 2C_4H_{8\,(g)} \qquad (D.1)$$

$$[Cu(C_6H_4ClO)_2(C_{11}H_7N_5OS)_2]_{(s)} + 95/2O_{2\,(g)} \rightarrow$$
$$CuCN_{(l)} + 33CO_{2\,(g)} + 11H_2O_{(g)} + 9NO_{2\,(g)} + 2SO_{2\,(g)} + Cl_{2\,(g)} \qquad (D.2)$$

The thermal decomposition of this complex occurs similarly with that of the compound (B). The nature of the final product was established by chemical elemental analysis (found: Cu, 70.84; C, 13.48; N, 15.77%; requires for CuCN: Cu, 70.95; C, 13.41; N, 15.64 %) and IR spectrum (which exhibits the characteristic vibration band ν(CN) at about 2100 cm^{-1}).

The DTG curves corresponding to all these reactions (A.1–D.2) show that these are not single, so the non-isothermal kinetic analysis was not performed.

Conclusions

- The main decomposition steps of two azo-derivatives and their Cu(II) complexes have been evidenced.
- In order to confirm the nature of some of the intermediate the IR spectra and chemical analyses were used.

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