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# THERMAL STABILITY STUDY OF SOME AZO-DERIVATIVES AND THEIR COMPLEXES
## Part 2. New azo-derivative pigments and their Cu(II) complexes

*M. Badea*[1*], *R. Olar*[1], *E. Cristurean*[1], *D. Marinescu*[1], *A. Emandi*[1], *P. Budrugeac*[2] *and E. Segal*[3]

[1]Department of Inorganic Chemistry, University of Bucharest, 90 Panduri St., 71267 Bucharest, Romania
[2]ICPE-CA, Research and Development Institute for Electrical Engineering, Spl. Unirii, 313, 74204 Bucharest, Romania
[3]Department of Physical Chemistry, University of Bucharest, 4-12 Elisabeta Blvd, Bucharest, Romania

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## Abstract

This paper deals with the investigation concerning the thermal stability of two new azo-derivatives and their Cu(II) complexes of type $[Cu(L^1)_2]$ and, respectively, $((C_4H_9)_4N)_2[Cu(L^2)_2]$. The thermal decomposition steps have been put in evidence. For the kinetically workable ones, the values of the activation energy *vs*. conversion degree were determined.

**Keywords:** azo-derivatives, Cu(II) complex, non-isothermal kinetics, thermal stability

## Introduction

The kinetics of the reactions studied by thermal analysis constitutes one of the most important aspects in the application of TA to the study and evaluation of materials [1, 2].

The thermal decomposition of the coordination compounds is used to obtain information on them as well as on the properties and the nature of intermediate and final products.

Azo-derivatives and their complexes are very important pigments for the synthetic leather and vinyl polymers. On the other hand, the azo-compounds are known to be involved in a number of biological reactions such as inhibition of DNA, RNA and protein synthesis, nitrogen fixation and carcinogenesis [3].

In the last years the interest regarding the synthesis and the characterisation of this type of compounds increased [4–7]. In a previous paper [8] we reported data

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[*] Author for correspondence: E-mail: mbadea@chem.unibuc.ro

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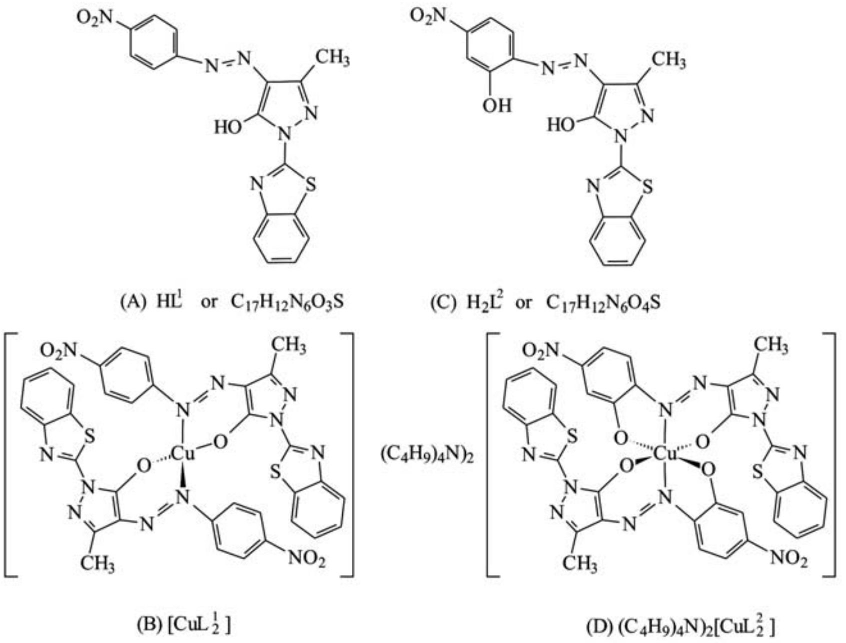
about the thermal behaviour of two azo-derivatives and their copper(II) complexes. We add now the corresponding data about other two new compounds of the same category (azo-derivatives complexes). The results presented here concern the decomposition steps, the analysis of intermediates and final residues and non-isothermal kinetic parameters (Scheme 1).



**Scheme 1** Compounds (A)–(D)

## Experimental

The compounds (A)–(D) have been synthesised and characterised by chemical analysis, electronic, vibration and EPR spectra [9]. 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 mmol $Cu(CH_3COO)_2{\cdot}H_2O$ was added drop-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 were recorded by help of a derivatograph, MOM Hungary, Paulik–Paulik–Erdey type in the temperature range 20–1000°C at heating rates in the range 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.

In order to evaluate the non-isothermal kinetic parameters, three isoconversional methods, namely Friedman [10], Flynn–Wall–Ozawa [11, 12] and Kissinger–Akahira–Sunose [13, 14] have been used.

## Results and discussion

The following solid compounds have been studied:

$$HL^1 \text{ or } C_{17}H_{12}N_6O_3S \qquad \text{(A)}$$

$$[CuL^1_2] \text{ or } CuC_{34}H_{22}N_{12}O_6S_2 \qquad \text{(B)}$$

$$H_2L^2 \text{ or } C_{17}H_{12}N_6O_4S \qquad \text{(C)}$$

$$((C_4H_9)_4N)_2[CuL^2_2] \text{ or } CuC_{66}H_{92}N_{14}O_8S_2 \qquad \text{(D)}$$

The results concerning the organic ligands and their Cu(II) complexes decomposition are comparatively presented below. Tables 1 and 2 summarise the thermogravimetric data.

**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 | $\Delta m_{exp}$ | $\Delta m_{calc}$ |
|---|---|---|---|---|---|
| $C_{17}H_{12}N_6O_3S$(A) | A.1 | endo | 290–370 | 32.78 | 32.36 |
| | A.2 | exo | 500–715 | 67.20 | 67.64 |
| $[CuC_{34}H_{22}N_{12}O_6S_2]$(B) | B.2 | endo | 115–230 | 30.07 | 29.94 |
| | B.3 | exo | 265–512 | 58.97 | 59.16 |
| Residue: CuCN | | | | 10.45 | 10.90 |

**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 | $\Delta m_{exp}$ | $\Delta m_{calc}$ |
|---|---|---|---|---|---|
| $C_{17}H_{12}N_5O_4S$(C) | C.1 | endo | 180–300 | 35.30 | 35.10 |
| | C.2 | exo | 400–645 | 51.05 | 51.77 |
| | C.3 | exo | 800–900 | 13.60 | 13.13 |
| $CuC_{66}H_{92}N_{14}O_8S_2$(D) | D.1 | exo | 160–315 | 31.78 | 31.92 |
| | D.2 | exo | 450–595 | 57.37 | 57.49 |
| | D.3 | exo | 700–770 | 3.76 | 3.89 |
| Residue: CuCN | | | | 7.09 | 6.79 |

### *Thermal decomposition of* $C_{17}H_{12}N_6O_3S$

The TG, T, DTG and DTA curves corresponding to the organic compound (A) heating in the 20–1000°C temperature range are presented in Fig. 1.

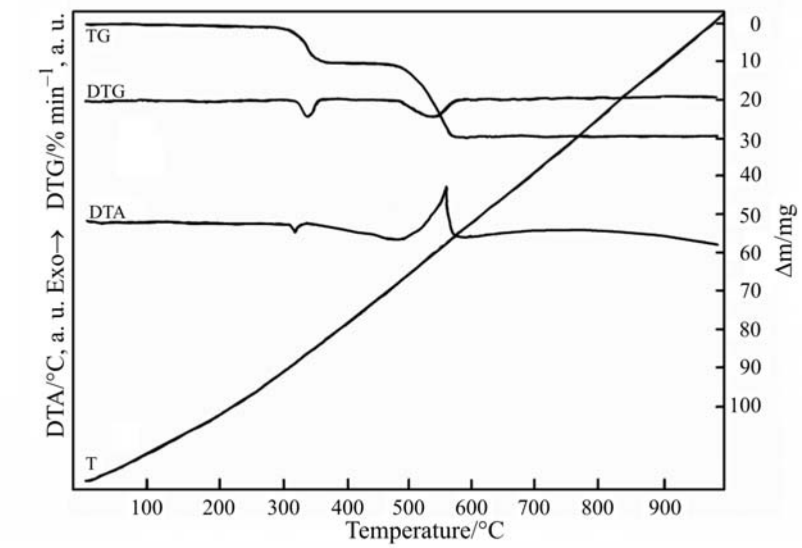


**Fig. 1** The TG, T, DTG and DTA curves of organic compounds HL$^1$ (sample mass: 30 mg)

According to the TG curve at progressive heating, the following decomposition steps have been evidenced:

$$C_{17}H_{12}N_6O_3S_{\ (s)} \xrightarrow{315°C} C_{11}H_7N_5OS_{\ (s)} + C_6H_5NO_{2\ (g)} \quad (A.1)$$

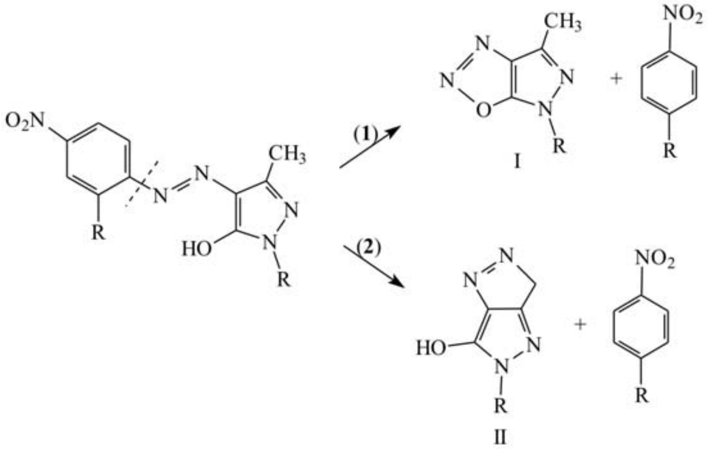
$$C_{11}H_7N_5OS_{\ (s)} + 20O_{2\ (g)} \xrightarrow{500-750°C} 11CO_{2\ (g)} + 7H_2O_{\ (g)} + 5NO_{2\ (g)} + SO_{2\ (g)} \quad (A.2)$$

In the chemical Eqs (A.1)–(A.2) the temperatures written above the arrows correspond at a heating rate of 2.8 K min$^{-1}$. The first decomposition step occurred in the temperature range 290–370°C (the maximum rate corresponds to the 315°C temperature) and it has a weak endothermic effect. This step corresponds to the $C_{arom}$–N bond cleavage, leading to the gaseous nitrobenzene formation (boiling point 210°C [15]). The rest of the organic component undergoes a cyclisation reaction by forming either a new oxodiazole or diazole ring as it is showed in Scheme 2.

The chemical elemental analysis was used in order to confirm the composition of the solid residue (found: C, 51.44; N, 27.42; H, 2.70; S, 12.31%; requires for $C_{11}H_7N_5OS$: C, 51.36; N, 27.23; H, 2.72; S, 12.45%).

The absence in IR spectrum of the reaction product, of the band corresponding to the stretching vibration ν(OH) represents a proof of the product (I) formation.

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



**Scheme 2** R=H:1-(2’-benzthiazolyl)-3-methyl-4-(azo)-phenyl)-pyrazol-5-one ($HL^1$), R=OH:1-(2’-benzthiazolyl)-3-methyl-4-(azo-2-hydroxy-phenylene)-pyrazol-5-one ($H_2L^2$)

For the reaction (A.1), which was proved to be kinetically workable, the kinetic analysis showed that the activation energy decreases progressively with an increase in the degree of conversion. By applying various isoconversional methods (Friedman (FR), Flynn–Wall–Ozawa (FWO) and Kissinger–Akahira–Sunose (KAS)) different values of the activation energy were obtained (Fig. 2). For a given value of α, $E_{FR}<E_{KAS}<E_{FWO}$.

The significant differences between $E_{FR}$ and $E$ calculated using the two integral methods appear because $E$ depends on α [16].

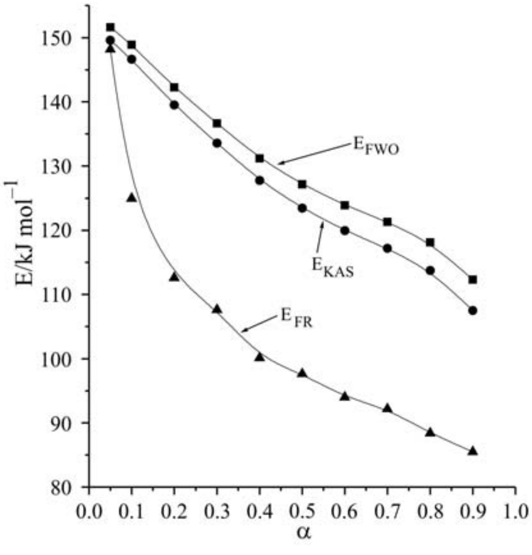


**Fig. 2** Plots of the activation energy *vs*. conversion degree for reaction (A.1)

*Thermal decomposition of [$CuC_{34}H_{22}N_{12}O_6S_2$]*

The TG and DTG curves (Fig. 3) indicate that the thermal decomposition occurs through the following steps:

$$[CuC_{34}H_{22}N_{12}O_6S_2]_{(s)} \xrightarrow{180°C} [CuC_{22}H_{12}N_{10}O_2S_2]_{(s)} + 2C_6H_5NO_{2\,(g)} \quad (B.1)$$

$$[CuC_{22}H_{12}N_{10}O_2S_2]_{(s)} + 34O_{2\,(g)} \xrightarrow{265–512°C} CuCN_{(l)} + 21CO_{2\,(g)} + 6H_2O_{(g)} + \\ + 9NO_{2\,(g)} + 2SO_{2\,(g)} \quad (B.2)$$

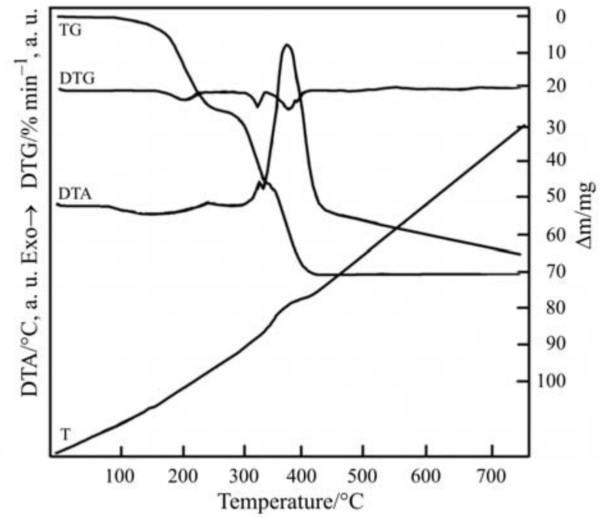
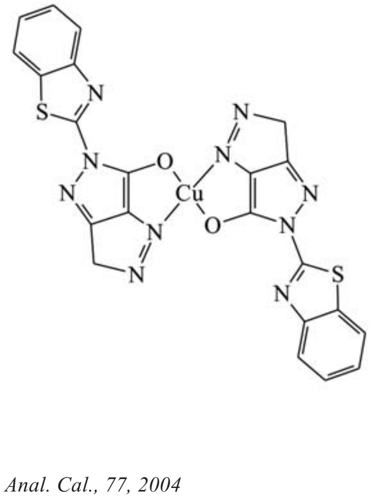
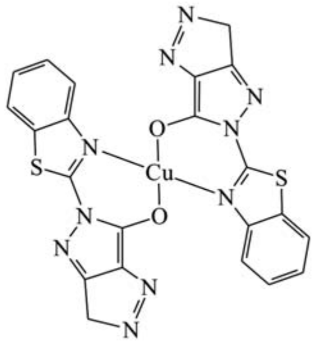


**Fig. 3** The TG, T, DTG and DTA curves of [$CuC_{34}H_{22}N_{12}O_6S_2$] (sample mass: 78 mg)

The first decomposition step was performed in 115–230°C temperature range and it is almost similar with the reaction (A.1). This step also contains the nitrobenzene elimination. In the left complex for each ligand is closed a new diazole ring. The probable formulae for this new complex are presented below:



or



The reaction (B.2) occurs in several steps that are difficult to separate; all exhibit an exothermal effect. The final product of the thermal decomposition is CuCN (*m.p.* 473°C), which is very stable (*b.p.*>1300°C) [17]. The nature of the final product was established by chemical elemental analysis (found: Cu, 70.80; C, 13.53; N, 15.82%; 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 $cm^{-1}$).

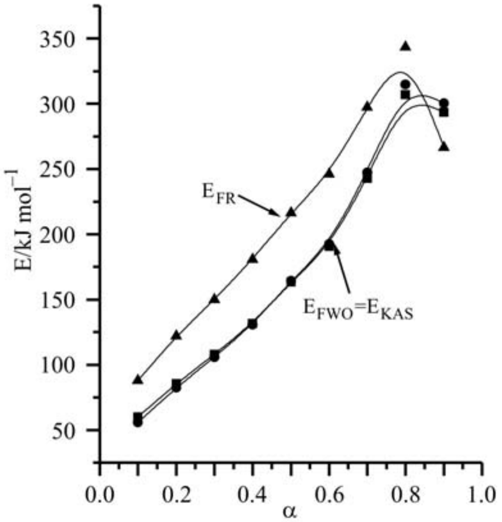


**Fig. 4** Plots of the activation energy *vs*. conversion degree for reaction (B.1)

As in the former case, the decomposition step that behaves as a single step is (B.1). The values of the activation energy of this reaction for different values of α are shown in Fig. 4. For a given value of α, $E_{FR}>E_{KAS}\approx E_{FWO}$.

*Thermal decomposition of* $C_{17}H_{12}N_6O_4S$

Despite the fact that this compound differs from (*A*) only by a phenolic group, the decomposition steps are different.

According to the heating curves (Fig. 5), thermal decomposition occurs according to the following steps:

$$C_{17}H_{12}N_6O_4S_{(s)} \xrightarrow{180\text{–}300°C} C_{11}H_7N_5OS_{(s)}+C_6H_5NO_{3\,(g)} \tag{C.1}$$

$$xC_{11}H_7N_5OS_{(s)}+57x/2O_{2(g)} \xrightarrow{400\text{–}645°C} (CN)_{2x\,(s)}+9xCO_{2\,(g)}+7x/2H_2O_{(g)}+ \\ +3xNO_{2\,(g)}+xSO_{2\,(g)} \tag{C.2}$$

$$(CN)_{2x\,(l)}+4xO_{2\,(g)} \xrightarrow{800\text{–}900°C} 2xCO_{2\,(g)}+2xNO_{2\,(g)} \tag{C.3}$$

The first endothermic step corresponds to a complex process in which occurs the cleavage of C–N bond, the formation of diazole ring and also the volatilisation of

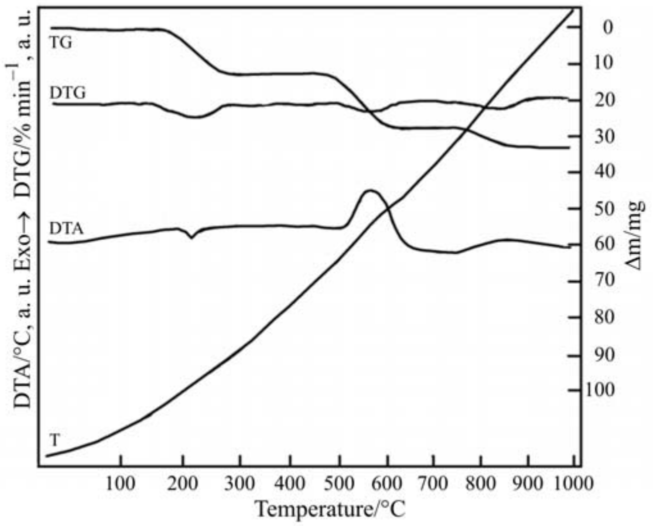


**Fig. 5** The TG, T, DTG and DTA curves of organic compounds $H_2L^2$ (sample mass: 34 mg)

4-nitrophenol (the 4-nitrophenol can be eliminated as it is or its oxidative degradation may occur, its boiling temperature being *b.p.* 279°C [15]).

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

The solid residue obtained after this step, which according to the analytical and IR data is the paracyanide (found: C, 45.98; N, 53.92%; requires for $(CN)_{2x}$: C, 46.15; N, 53.85; %), ν(CN): 2110 cm$^{-1}$), undergoes further depolymerisation. The dicyanide which results in this process undergoes then an oxidative degradation at temperatures higher than 800°C.

### *Thermal decomposition of $CuC_{66}H_{92}N_{14}O_8S_2$*

The heating curves exhibited the following thermal decomposition steps (Fig. 6):

$$\mathrm{CuC_{66}H_{92}N_{14}O_8S_{2\,(s)}}\xrightarrow{160-315^\circ\mathrm{C}}\mathrm{CuC_{34}H_{22}N_{12}O_8S_{2\,(s)}}+2\mathrm{C_{12}H_{27}N_{\,(g)}}+\mathrm{C_4H_{8\,(g)}} \quad \text{(D.1)}$$

$$x\mathrm{CuC_{34}H_{22}N_{12}O_8S_{2\,(s)}}+87x/2\mathrm{O_2}\xrightarrow{450-595^\circ\mathrm{C}}x\mathrm{CuCN_{(l)}}+(\mathrm{CN})_{2x\,(s)}+31x\mathrm{CO_{2\,(g)}}+$$

$$+11\mathrm{H_2O_{\,(g)}}+9x\mathrm{NO_{2\,(g)}}+2x\mathrm{SO_{2\,(g)}} \quad \text{(D.2)}$$

$$x\mathrm{CuCN_{(l)}}+(\mathrm{CN})_{2x\,(s)}+4x\mathrm{O_{2\,(g)}}\xrightarrow{700-770^\circ\mathrm{C}}x\mathrm{CuCN_{(l)}}+2x\mathrm{CO_{2(g)}}+2x\mathrm{NO_{2\,(g)}} \quad \text{(D.3)}$$

The thermal decomposition of this complex occurs similar with those of organic ligand, excepting the fact that, however even in the first step the cleavage of C–N bond occurs, and the 4-nitrophenolate resulted ion still remains coordinated to the metal ion. This step occurs in the same time with the thermal decomposition of tetrabutylammonium ion in tributylamine and butane [15]. The nature of the residue

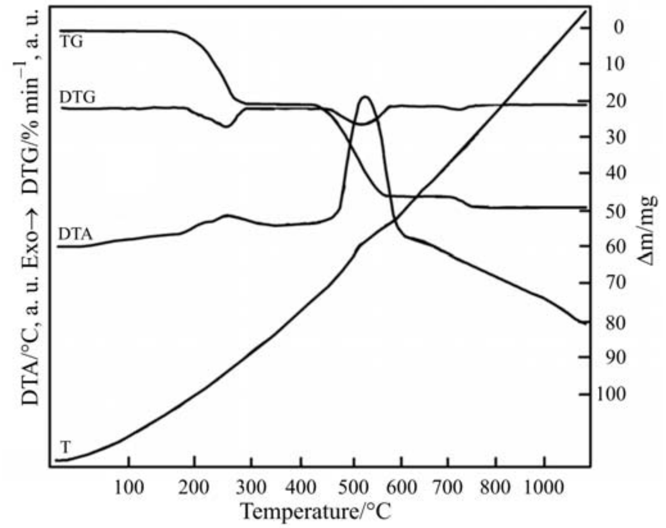


**Fig. 6** The TG, T, DTG and DTA curves of $CuC_{66}H_{92}N_{14}O_8S_2$ (sample mass: 53 mg)

was supported by chemical elemental analysis (found: Cu, 7.80; C, 47.73; N, 19.73; H, 2.50; S, 7.58%; requires for $CuC_{34}H_{22}N_{12}O_8S_2$: Cu, 7.44; C, 47.80; H, 2.58; N, 19.68; S, 7.50%).

Next steps, which are accompanied by exothermic effects, correspond to the oxidative degradation of the organic component and to the reduction of the resulted copper complex ion to copper cyanide.

As the DTG curve corresponding to the reactions (C.1)–(D.3) shows that these are not simple reactions, the non-isothermal kinetic analyses were not performed on them.

## 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 analysis were used.
- The thermal analysis has shown that these compounds are stable up to 115–290°C. As a consequence of this behaviour, they are suitable as dyes in high temperature processes as printing and photocopying.
- For two kinetically workable steps, a kinetic study, using three isoconversional methods was done.
- The significant differences between $E_{FR}$ and $E$ calculated using the two integral methods appear because $E$ depends on $\alpha$. In this case the Friedman method is recommended because the other integral methods are based on the mathematic relations which consider that the activation parameters do not depend on $\alpha$.
- For the two decomposition steps, (A.1) and (B.1), which occur with the nitrobenzene elimination, a high difference between the temperature ranges was

observed. Moreover, the variation of activation energy values with $\alpha$ is reverse. This behaviour could be explained considering different reaction mechanisms for these steps. This could be determined by the fact that the copper ion acts as catalyst in thermal decomposition of the complex compound.

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