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Thermal stability and non-isothermal decomposition kinetics of three coordination compounds of copper(II)

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Abstract

Results concerning the thermal behavior of three coordination compounds of Cu(II) with the ligand 2-amino-5-mercapto-1,3,4-thiadiazole are reported. Values of the non-isothermal kinetic parameters have been determined for some of the decomposition steps.

Keywords: Thermal stability; Copper(II); Non-isothermal kinetics

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1. Introduction

Following our earlier research on the thermal stability of coordination compounds [1–3], this paper is concerned with the thermal behavior of three Cu(II) complexes with 2 amino-5-mercapto-1,3,4-thiadiazole: **I**, **II** and **III**.

According to literature data, investigations into derivatives of 1,3,4-thiadiazole have shown that they act as inhibitors for the enzyme carbonic anhydrase [4, 5]. When such compounds are used as coordination ligands, this inhibition is not only preserved but in same cases amplified [6].

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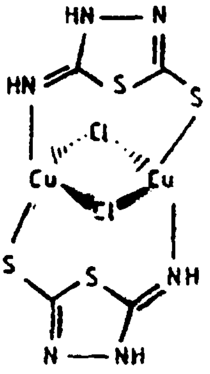
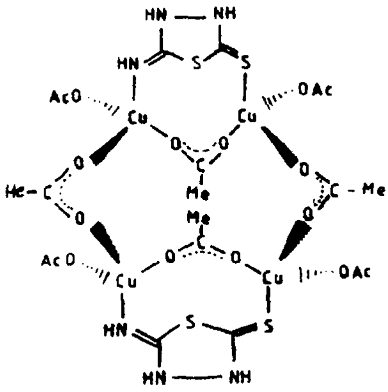


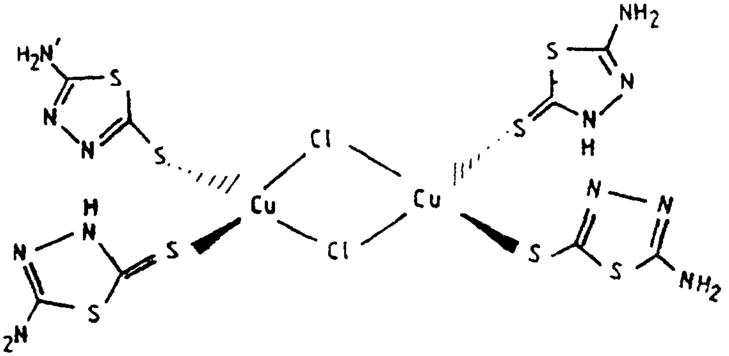
I

$[Cu_2C_4H_4N_6S_4Cl_2]$



II

$[Cu_4C_{20}H_{30}O_{16}N_6S_4]$



III

$[Cu_2C_8H_{10}N_{12}S_8Cl_2]$

2. Experimental

The coordination compounds **I**, **II** and **III** were synthesized as amorphous powders (no peaks on X-ray diffractograms) and characterized by chemical analysis, electron paramagnetic resurance, and electronic and vibrational spectroscopy [6].

The heating curves (TG, *T*, ATD and DTG) were recorded in a MOM (Budapest) derivatograph, type Paulik-Paulik-Erdey, in a static air atmosphere using various heating rates in the range 2–10 K min^{-1}.

X-ray diffractograms using chromium K_α radiation were obtained on a Phillips P.W. 1400 diffractometer.

In order to evaluate the kinetic parameters, three methods were applied: the Coats–Redfern [7], the Flynn–Wall (for constant heating rate) [8], and the Urbanovici and Segal [9], modification of the Coats–Redfern method.

The experimental data were processed automatically using a program written in basic by Dragoe and Segal [10]. Once the non-isothermal kinetic parameter values are known, the program allows for regeneration of the TG curves in (α, T°C) coordinates, where α is the fractional extent of reaction, and for addition of the experimental points.

3. Results and discussion

3.1. *Decomposition of* $[Cu_2C_4H_4N_6S_4Cl_2]$ (**I**)

From the mass losses on the TG and DTG curves, the following decomposition steps with progressive temperature increase can be deduced

$$[Cu_2C_4H_4N_6S_4Cl_2](s) + 2O_2(g) \xrightarrow{90^\circ C} [C_4H_4N_4S_4Cl_2](s) + 2NO_2(g) \quad (1)$$

$$[Cu_2C_4H_4N_4S_4Cl_2](s) + 2O_2(g) \xrightarrow{210^\circ C} [Cu_2C_4H_4N_4S_2Cl_2](s) + 2SO_2(g) \quad (2)$$

$$[Cu_2C_4H_4N_4S_2Cl_2](s) + 5O_2(g) \xrightarrow{270^\circ C} [Cu_2C_2N_2S_2Cl_2](s) + 2CO_2(g) + 2NO_2(g) + 2H_2O(g) \quad (3)$$

$$[Cu_2C_2N_2S_2Cl_2](s) + 4O_2(g) \xrightarrow{450^\circ C} 2CuS(s) + 2NO_2(g) + 2CO_2(g) + Cl_2(g) \quad (4)$$

$$2CuS(s) + 3.5Os(g) \xrightarrow{525^\circ C} CuO(s) + CuSO_4(s) + SO_2(g) \quad (5)$$

$$CuO(s) + CuSO_4(s) \xrightarrow{735^\circ C} 2CuO(s) + SO_3(g) \quad (6)$$

The temperature written above the arrows correspond to the maximum decomposition rate as shown by the peaks of the DTG curves, recorded at $\beta = 2.98\ K\ min^{-1}$.

The existence of the intermediate products of reactions (1)–(3) have been confirmed by the elemental analysis, and electronic (UV–VIS) and IR spectra. The presence of CuS and CuO as solid residues of reactions (4)–(6) was confirmed by X-ray diffractograms.

Kinetic analysis of decomposition steps (1) and (2) is possible.

Table 1
Values of the non-isothermal kinetic parameters of reaction (1) at $\beta = 2.98\ K\ min^{-1}$

Method	n	E/(kJ mol^{-1})	A/(s^{-1})	$\lvert r \rvert$[a]
Coats–Redfern	1.7	46.4	9.73×10^3	0.997
Flynn–Wall	1.6	47.7	2.68×10^4	0.998
Modified Coats–Redfern	1.6	45.6	7.95×10^3	0.997

[a] Correlation coefficient of linear regression.

Table 2
Values of the non-isothermal kinetic parameters of reaction (2) at $\beta = 2.98$ K min^{-1}

Method	n	E/(kJ mol^{-1})	A/(s^{-1})	$\lvert r \rvert$[a]
Coats–Redfern	1.2	76.9	1.05×10^5	0.998
Flynn–Wall	1.2	80.7	4.30×10^5	0.999
Modified Coats–Redfern	1.2	79.0	2.13×10^5	0.999

[a] Correlation coefficient of linear regression.

The values of the kinetic rate parameters; reaction order n, activation energy E and the pre-exponential factor A, for these single steps, are listed in Tables 1 and 2. The results in Tables 1 and 2 show a good agreement between the values of the rate parameters obtained by all three methods applied.

3.2. *Decomposition of* $[Cu_4C_{20}H_{30}O_{16}N_6S_4]$ (II)

The presence of acetate anions as ligand with the Cu(II) complex leads to a different coordination compound and thus to a different thermal behavior.

According to the heating curves, recorded at $\beta = 2.84$ K min^{-1}, this compound undergoes decomposition in the following steps

$$[Cu_4C_{20}H_{30}O_{16}N_6S_4](s) + 3O_2(g) \xrightarrow{80^\circ C} [C_4C_{18}H_{26}O_{16}N_6S_4](s) + 2CO_2(g) + 2H_2O(g) \quad (7)$$

$$[Cu_4C_{18}H_{26}O_{16}N_6S_4](s) + 3O_2(g) \xrightarrow{160^\circ C} [Cu_4C_{16}H_{22}O_{16}N_6S_4](s) + 2CO_2(g) + 2H_2O(g) \quad (8)$$

$$[Cu_4C_{16}H_{22}N_6S_4](s) + 3O_2(g) \xrightarrow{190^\circ C} [C_4C_{14}H_{18}O_{16}N_6S_4](s) + 2CO_2(g) + 2H_2O(g) \quad (9)$$

$$[Cu_4C_{14}H_{18}O_{16}N_6S_4](s) + 3O_2(g) \xrightarrow{230^\circ C} [Cu_4C_{12}H_{14}O_{16}N_6S_4](s) + 2CO_2(g) + 2H_2O(g) \quad (10)$$

In the first four decomposition steps above, the acetate anions decompose stepwise to form formate anions. The existence of intermediates was confirmed by chemical analysis and IR spectra.

$$[Cu_4C_{12}H_{14}O_{16}N_6S_4](s) + 4.5O_2(g) \xrightarrow{280^\circ C} [Cu_4C_8H_4O_8N_4S_4](s) + 4CO_2(g) + 2NO_2(g) + 5H_2O(g) \quad (11)$$

$$[Cu_4C_8H_4O_8N_4S_4](s) + 9O_2(g) \xrightarrow{425^\circ C} 4CuS(s) + 4NO_2(g) + 8CO_2(g) + 2H_2O(g) \quad (12)$$

$$2CuS(s) + 3.5O_2(g) \xrightarrow{530^\circ C} CuSO_4(s) + CuO(s) + SO_2(g) \quad (13)$$

$$CuSO_4(s) + CuO(s) \xrightarrow{795^\circ C} 2CuO(s) + SO_3(g) \quad (14)$$

The presence of CuS and CuO as solid decomposition products of reactions (12) and (14), respectively, was confirmed from X-ray diffractograms. Also, the existence of $CuSO_4$ mixed with CuO in the solid residue of reaction (13) was confirmed by chemical analysis and IR spectra.

The single decomposition steps (7) and (8) can be analysed. The values of the kinetic parameters for these steps are listed in Tables 3 and 4.

3.3. *Decomposition of* $[Cu_2C_8H_{10}N_{12}S_8Cl_2]$ (**III**)

The decomposition steps are similar to those of the compound $[Cu_2C_4H_4N_6S_4Cl_2]$, although the molar ratio, Cu: thiadiazolic ligand, is different.

By examining the thermal curves (recorded at $\beta = 2.70\,K\,min^{-1}$) it is possible to distinguish the following decomposition steps

$$[Cu_2C_8H_{10}N_{12}S_8Cl_2](s) + 5O_2(g) \xrightarrow{155^\circ C} [Cu_2C_8H_6N_8S_8Cl_2](s) + 4NO_2(g) + 2H_2O(g) \quad (15)$$

Table 3
Values of the non-isothermal kinetic parameters of reaction (7) at $\beta = 2.84\,K\,min^{-1}$

Method	n	$E/(kJ\,mol^{-1})$	$A/(s^{-1})$	$\|r\|$[a]
Coats–Redfern	2.0	48.9	2.05×10^4	0.995
Flynn–Wall	2.0	52.3	1.11×10^5	0.996
Modified Coats–Redfern	2.0	50.2	3.71×10^4	0.995

[a] Correlation coefficient of linear regression.

Table 4
Values of the non-isothermal kinetic parameters of reaction (8) at $\beta = 2.84\,K\,min^{-1}$

Method	n	$E/(kJ\,mol^{-1})$	$A/(s^{-1})$	$\|r\|$[a]
Coats–Redfern	1.2	92.0	1.61×10^6	0.996
Flynn–Wall	1.1	92.4	2.20×10^6	0.997
Modified Coats–Redfern	1.1	91.1	1.36×10^6	0.997

[a] Correlation coefficient of linear regression.

$$[Cu_2C_8H_6N_8S_8Cl_2](s) + 4O_2(g) \xrightarrow{335^\circ C} [Cu_2C_8H_6N_8S_4Cl_2](s) + 4SO_2(g) \quad (16)$$

$$[Cu_2C_8H_6N_8S_4Cl_2](s) + 15.5O_2(g) \xrightarrow{450^\circ C} [Cu_2C_2N_2S_2Cl_2](s) + 6CO_2(g) + 2SO_2(g) + 6NO_2(g) + 3H_2O(g) \quad (17)$$

$$[Cu_2C_2N_2S_2Cl_2](s) + 4O_2(g) \xrightarrow{520^\circ C} 2CuS(s) + Cl_2(g) + 2NO_2(g) + 2CO_2(g) \quad (18)$$

$$2CuS(s) + 3.5O_2(g) \xrightarrow{545^\circ C} CuSO_4(s) + CuO(s) + SO_2(g) \quad (19)$$

$$CuSO_4(s) + CuO(s) \xrightarrow{725^\circ C} 2CuO(s) + SO_3(g) \quad (20)$$

The intermediates were isolated and characterized by chemical analysis, and IR and electronic (UV–VIS) spectra.

Table 5
Values of the non-isothermal kinetic parameters of reaction (15) at $\beta = 2.70$ K min^{-1}

Method	n	E/(kJ mol^{-1})	A/(s^{-1})	$\lvert r\rvert$[a]
Coats–Redfern	1.4	69.0	6.26×10^7	0.997
Flynn–Wall	1.4	70.7	1.53×10^8	0.997
Modified Coats–Redfern	1.3	69.8	9.70×10^7	0.996

[a] Correlation coefficient of linear regression.

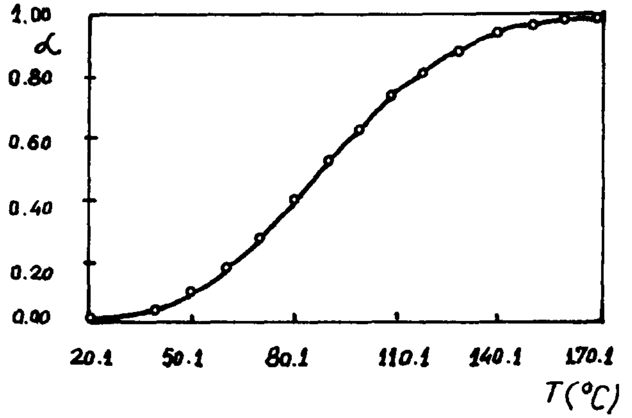


Fig. 1. Regenerated thermogravimetric curve using coordinates α, T(°C) for reaction (1): —, calculated curve, ○, experimental points. Curves were regenerated using non-isothermal kinetic parameters determined by the Coats–Redfern method.

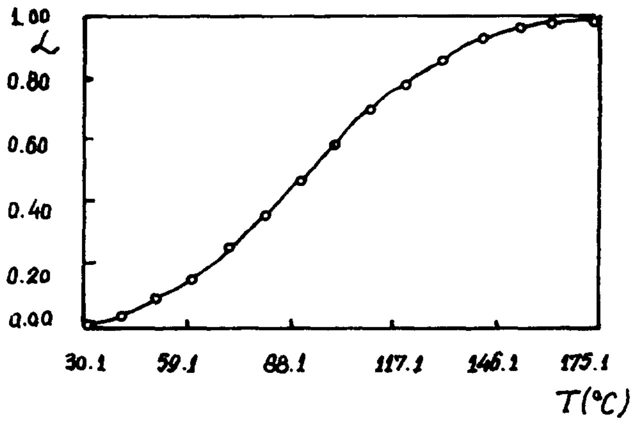


Fig. 2. Regenerated thermogravimetric curve using coordinates α, T(°C) for reaction (7): —, calculated curve; ○, experimental points. Curves were regenerated using non-isothermal kinetic parameters determined by the Coats–Redfern method.

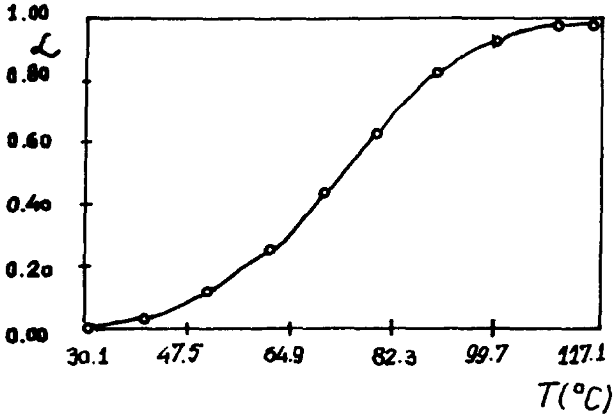


Fig. 3. Regenerated thermogravimetric curve using coordinates α, T(°C) for reaction (15): —, calculated curve; ○, experimental points. Curves were regenerated using non-isothermal kinetic parameters determined by the Coats–Redfern method.

Table 5 gives the values of the non-isothermal kinetic parameters of reaction (15).

Figs. 1, 2 and 3 show the plots of regenerated TG curves for reactions (1), (7) and (15). From these figures, it can be seen that the experimental points fit well with the calculated curves, thus confirming the accuracy of the determined values of the non-isothermal kinetic parameters and the methods used to evaluate them.

4. Conclusions

The main decomposition steps of the three coordination compounds $[Cu_2C_4H_4N_6S_4Cl_4]$, $[Cu_4C_{20}H_{30}O_{16}N_6S_4]$ and $[Cu_2C_8H_{10}N_{12}S_8Cl_2]$ have been outlined. For the single decomposition steps, a non-isothermal kinetic analysis was performed. The values of the kinetic parameters obtained using three different methods are in satisfactory agreement.

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