*Journal of Thermal Analysis and Calorimetry, Vol. 88 (2007) 3, 637–640*

# KINETIC OF DECOMPOSITION OF SOME COMPLEXES UNDER NON-ISOTHERMAL CONDITIONS

*Gabriela Vlase*[1], *T. Vlase*[1*], *Ramona Tudose*[2], *Otilia Costişor*[2] *and N. Doca*[1]

[1]West University of Timişoara, Research Center for Thermal Analysis in Environmental Problems, Str. Pestalozzi No. 16, Timişoara, 300115, Romania
[2]Institute of Chemistry Timişoara, B-dul M. Viteazul, No. 24, Romania

Kinetics of thermal decomposition of three structurally similar complexes $Co_2Cu(C_2O_4)_3$ (R-diam)$_2$, where *R* is ethyl, 1,2-propyl or 1,3-propyl, was studied under non-isothermal conditions and nitrogen dynamic atmosphere at heating rates of 5, 7, 10, 12 and 15 K min$^{-1}$.

For data processing the Flynn–Wall–Ozawa and a modified non-parametric kinetic methods were used. By both methods the activation energy are in the range of 97–102 kJ mol$^{-1}$. The formal kinetic is $r=k\alpha(1-\alpha)^2$. Also a compensation effect between ln*A* and *E* was evidenced. The kinetic analysis lead to the conclusion of an identic decomposition mechanism by a single step process.

***Keywords:*** *non-isothermal kinetics, thermal decomposition, three-nuclear complexes*

## Introduction

The complexes are adequate precursors for obtaining supported catalysts, especially due to their low decomposition temperature. By polynuclear complexes, it is a supplementary advantage, namely the designed and/or desired intermetallic distance [1].

The non-isothermal analysis is frequently used to characterize the thermal decomposition of catalyst precursors. But the informations on the intimate reaction mechanism depends on the data processing strategy used for obtaining the kinetic parameters [2–6].

In the present paper a kinetic study on the decomposition under non-isothermal conditions of three polynuclear complexes was performed. The complexes were cobalt and copper containing polynuclear–polydentate complexes, with oxalate as common ligand and low diamine as specific ligands.

The kinetic analysis was performed by the Flynn–Wall [7] and Ozawa [8] method (FWO) and by a non-parametric kinetic method (NPK). The FWO method, in the model-free-invariant version, is a large-accepted method [9] of data processing in non-isothermal kinetic. The NPK method, initial suggested by Nomen and Sempere [10, 11], was modified and widely used for kinetic analysis of complex processes [6, 12–14].

## Experimental

The studied complex where three center complexes, Co/Cu/Co, whit the composition

| | |
|---|---|
| $OD_4$ | $Co_2Cu(C_2O_4)_3$(Et-diAm)$_2$ |
| $OD_{22}$ | $Co_2Cu(C_2O_4)_3$(Pr-1,2-diAm)$_2$ |
| $OD_{31}$ | $Co_2Cu(C_2O_4)_3$(Pr-1,3-diAm)$_2$ |

where $C_2O_4$ means the oxalate anion, Et-diAm, the ethylene-diamino ligand and Pr-x,y-diAm means the propylene-1,2respectively 1,3-diamino ligand.

The synthesis and physico-chemical characterization of the complexes were reported earlier [15].

The thermoanalytical data were obtained on a Perkin-Elmer Diamond devices, in nitrogen dynamic atmosphere (100 mL min$^{-1}$), so no thermooxidative degradation occurs. Heating rates of 5, 7, 10, 12 and 15 K min$^{-1}$ and Al crucibles were used.

The degradation degree of the compounds was studied by drawing up the FTIR spectra before and after the thermal treatment on a Perkin-Elmer Spectrum 100 device and the U-ATR$^{TM}$ technique was used.

## Results and discussion

Some typical TG/DTG curves are depicted in Fig. 1. The thermal behavior of the three compounds is similar and the mass loss is rather the same, i.e. 56% by $OD_4$, 58% by $OD_{22}$ and 57% by $OD_{31}$, respectively.

By the spectra for the compound before the thermal treatment remarkable are the peaks at 1330–1440 and 1550–1650 cm$^{-1}$, characteristic for the $\upsilon_S$, respectively $\upsilon_{as}$ vibrations of the carboxylate group [16] (Fig. 2). The total destroying of the samples is demonstrated

---

[*] Author for correspondence: tvlase@cbg.uvt.ro

*1388–6150/$20.00*

*Akadémiai Kiadó, Budapest, Hungary*
*Springer, Dordrecht, The Netherlands*

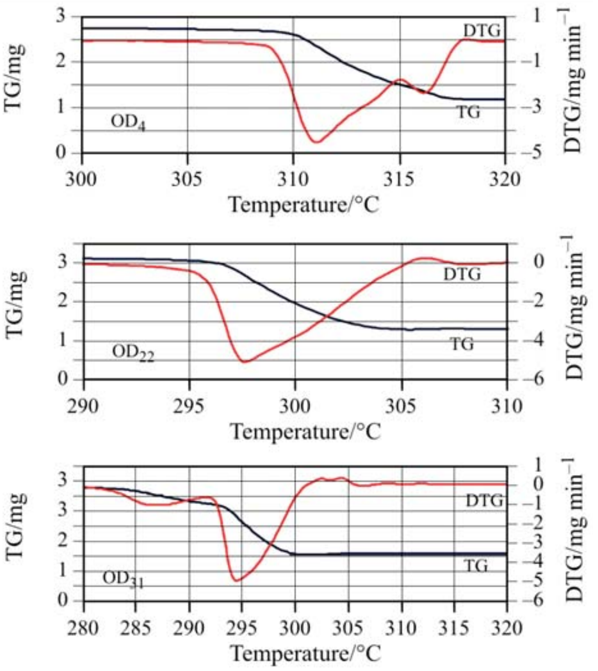

**Fig. 1** TG/DTG curves by 15 K min$^{-1}$

by the straight line in the range of 600–1800 cm$^{-1}$, observed by the FTIR spectra of all the three compounds after heating at 500°C.

The FWO isoconversional method is based on the rate equation written like

$$\ln\beta=\ln\left[A\frac{f(\alpha)}{\mathrm{d}\alpha/\mathrm{d}t}\right]_{\alpha}-\frac{E}{RT} \tag{1}$$

where α is the degree of conversion, β – the heating rate, $A$ – the pre-exponential factor in the Arrhenius equation, $E$ – the activation energy, $R$ – the gas constant, $T$ – the temperature, and $f(\alpha)$ – the conversion function. In the model-free version of the FWO method it is not necessary to give any explicit form of $f(\alpha)$.

By plotting ln(β) *vs.* 1/$T$ at a certain conversion degree, a straight line with the slope-$E/R$ is obtained. The data are presented in Table 1.

There is a small variation of $E$ *vs.* α, so that a main value of the activation energy, became significant.

The very near values obtained are in agreement with the very similar molecular structure. The difference from 98 to 102 kJ mol$^{-1}$ of the activation energy (less than 4%) is not necessary in connection with the 1,2 respectively 1,3 bonding of the diamino ligand.

This relative homogeneity in the values of the activation energy, a small variation of $E$ *vs.* α and the presence of just one significant DTG peak in the decomposition range are the first indications for a single step process.

In order to verify this hypothesis, we used the modified NPK method [6, 12–14] for the data processing. This method is able:

- to separate the temperature, respective conversion contribution to the reaction rate;
- to discriminate between one or more processes involved into a decomposition step.

By this method, the experimental points obtained at different heating rates β, are represented in a 3D space, respectively temperature $T$, conversion α and reaction rate dα/d$t$. These points are interpolated as a continuous surface described by

$$\beta\mathrm{d}\alpha/\mathrm{d}t=f(T)g(\alpha) \tag{2}$$

where $f(T)$ is the function for the temperature dependence and $g(\alpha)$ is the function for the conversion dependence.

This surface can by discretized and organized as a square i*j matrix M:

$$\mathrm{M}=\{\mathrm{m}_{i,j}\}=\{f(T_j)g(\alpha_i)\} \tag{3}$$

Applying the singular value decomposition (SVD) algorithm [17], the matrix M is decomposed according to:

$$\mathrm{M}=\mathrm{U}(\mathrm{diags})\mathrm{V}^{\mathrm{T}} \tag{4}$$

A vector $u_1$ given by the first column of the matrix U is analyzed *vs.* α in order to determine the conversion function.

We suggest the Šesták–Berggren [18] equation:

$$g(\alpha)=\alpha^{\mathrm{m}}(1-\alpha)^{\mathrm{n}} \tag{5}$$

A similar vector $v_1$, corresponding to the matrix V, is searched for an Arrhenius type temperature dependence.

If the thermal degradation is a result of two simultanous processes 1 and 2, it means that the matrix M became

$$\mathrm{M}=\mathrm{M}_1+\mathrm{M}_2 \tag{6}$$

and, consequently, two sets of kinetic parameters $E$, $A$, $m$ and $n$ will be obtained. The contribution of each process to the observed experimental dα/dt variation

**Table 1** Activation energy, kJ mol$^{-1}$ *vs.* conversion, by FWO method

| Compound | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 | main |
|---|---|---|---|---|---|---|---|---|---|---|
| OD$_4$ | 101.6 | 100.7 | 99.6 | 98.9 | 97.9 | 96.2 | 94.7 | 92.7 | 91.5 | 97.1 |
| OD$_{22}$ | 103.5 | 101.9 | 101.0 | 99.6 | 98.0 | 96.8 | 95.2 | 93.6 | 91.3 | 97.9 |
| OD$_{31}$ | 108.2 | 107.0 | 105.4 | 103.8 | 102.7 | 100.5 | 98.7 | 97.2 | 95.1 | 102.1 |

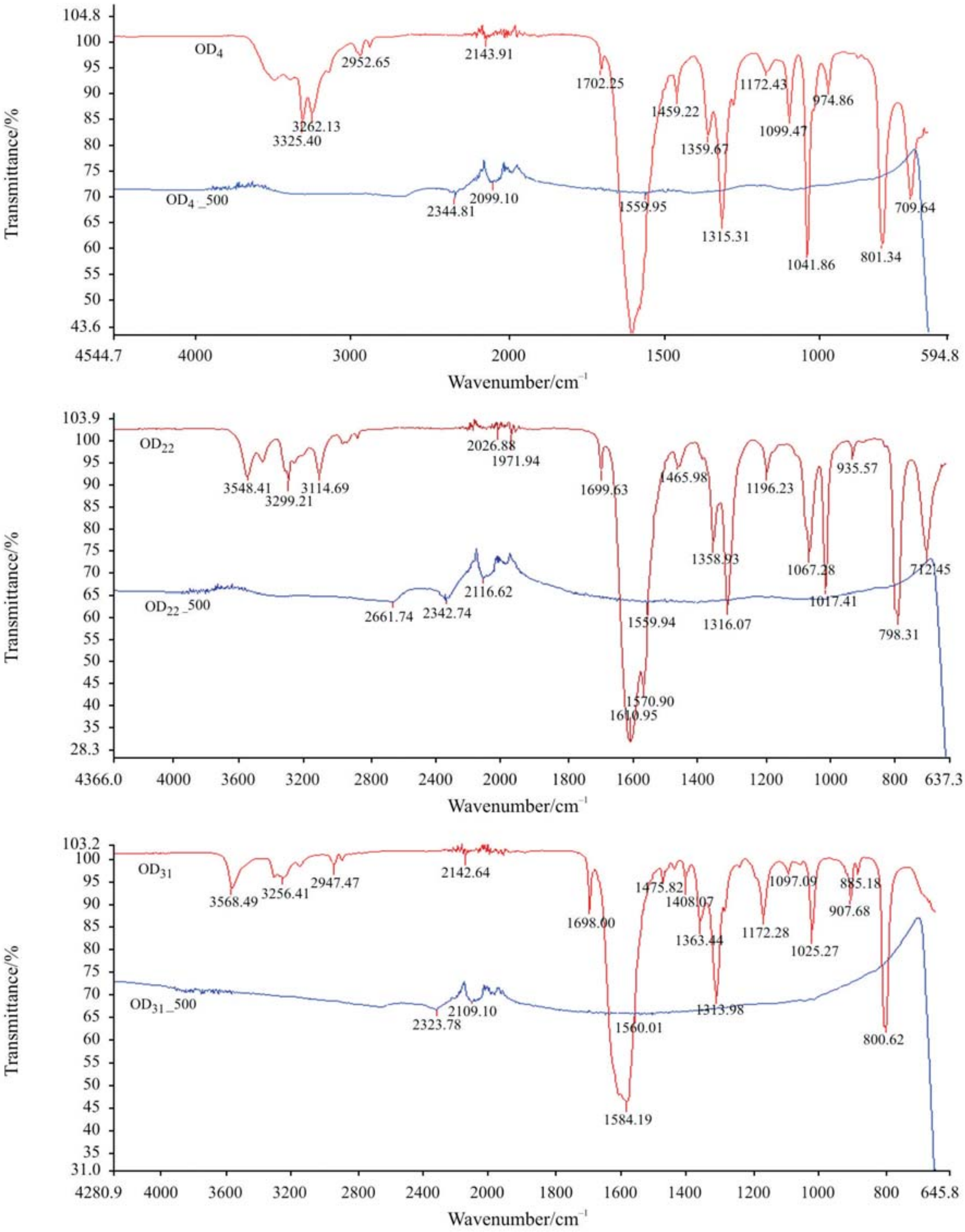

**Fig. 2** The FTIR spectra for complexes obtained before and after heating at 500°C

is expressed by the explained variance λ, so that $\lambda_1+\lambda_2=100\%$.

The data obtained by the NPK method are systematized in Table 2. The very high value of the explained variance (λ>90%) is a consistent argument for considering the decomposition in nitrogen as a single step process.

The values obtained for the activation energy are practically the same with those one by FWO method (column main *E* in Table 1). This is relevant, because the FWO method is well-established for single step processes [9].

The similar structure of the studied compounds lead to the idea of an identic decomposition mechanism. Two supplementary kinetic arguments are in support of the this opinion (the same formal kinetic equation, i.e. the *m* and *n* parameters of Eq. (5)).

**Table 2** Kinetic parameters by NPK method

| Compound | λ | $E$/kJ mol$^{-1}$ | $A$/min$^{-1}$ | $m$ | $n$ |
|---|---|---|---|---|---|
| $OD_4$ | 91.6 | 97.2 | $1.474\cdot10^8$ | 2/3 | 2 |
| $OD_{22}$ | 97.8 | 96.7 | $7.781\cdot10^8$ | 1 | 2 |
| $OD_{31}$ | 98.2 | 102.4 | $3.323\cdot10^9$ | 1 | 2 |

## Conclusions

By performing the thermal decomposition of the structural similar complexes in nitrogen atmosphere, the ‘intrinsic’ thermal stability of the molecules was possible to be evidenced. A kinetic study allows a quantitative estimation of the thermal behavior.

The FWO method, a rather simple strategy of data processing, allows a good estimation of the thermal stability by the main value of the activation energy.

The more sophisticated NPK method furnish similar values for the activation energy. But due to its less speculative strategy, this method allows a separation between the temperatures, respective the conversion degree dependence of the reaction rate.

The good agreement between FWO and NPK method, as well as a very near variation of the activation energy *vs.* conversion is due to a single step decomposition process.

## References

1 D. L. Trimm, Design of Industrial Catalysts, Elsevier, Amsterdam 1980.
2 T. Vlase, G. Vlase and N. Doca, Thermochim. Acta, 379 (2001) 59.
3 T. Vlase, G. Vlase and N. Doca, Thermochim. Acta, 379 (2001) 65.
4 T. Vlase, G. Vlase, A. Chiriac and N. Doca, J. Therm. Anal. Cal., 72 (2003) 839.
5 T. Vlase, G. Vlase, A. Chiriac and N. Doca, J. Therm. Anal. Cal., 72 (2003) 847.
6 T. Vlase, G. Vlase, A. Chiriac and N. Doca, J. Therm. Anal. Cal., 80 (2005) 87.
7 I. H. Flynn and L. A. Wall, Polym. Lett., 4 (1966) 323.
8 T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881.
9 M. E. Brown, *et al.*, Thermochim. Acta, 355 (2000) 125.
10 R. Serra, R. Nomen and J. Sempere, J. Therm. Anal. Cal., 52 (1998) 923.
11 R. Serra, R. Nomen and J. Sempere, Thermochim. Acta, 316 (1998) 37.
12 T. Vlase, G. Vlase, N. Doca and C. Bolcu, J. Therm. Anal. Cal., 80 (2005) 59.
13 T. Vlase, G. Vlase and N. Doca, J. Therm. Anal. Cal., 80 (2005) 207.
14 T. Vlase, G. Vlase and N. Doca, J. Therm. Anal. Cal., 80 (2005) 425.
15. O. Costişor, C. Stănescu, S. Policec, P. Weinberger, J. Zang and W. Linert, Orient J. Chem., 13 (1997) 197.
16 R. M. Silverstein, G. Clayton Basster and T. Morrell, Spectrometric Identification of the Compounds, 5th Ed., John Wiley, 1995.
17 M. E. Wall, *et al.*, A Practical Approach to Microarray Data Analysis, Kluwer-Norwel, MA 2003, LNL LA-UR-02, pp. 91-109.
18 J. Šesták and G. Berggren, Thermochim. Acta, 3 (1971) 1.

Received: August 29, 2006

DOI: 10.1007/s10973-006-8020-5