Thermochimica Acta, 178 (1991) 241–248
Elsevier Science Publishers B.V., Amsterdam

ON THE THERMAL BEHAVIOUR OF TWO COORDINATION COMPOUNDS OF Ni(II) and Co(II)

MARILENA FERBINȚEANU and MARIUS ANDRUH

Department of Inorganic Chemistry, Faculty of Chemistry, University of Bucharest, Str. Dumbrava Roșie Nr. 23 Bucharest (Romania)

E. SEGAL

Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest, Bulevardul Republicii 13, Bucharest (Romania)

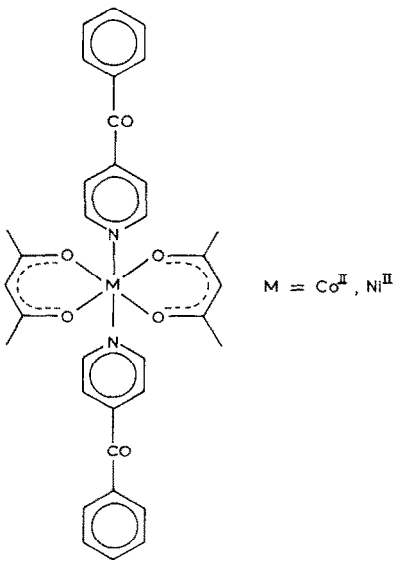
(Received 2 July 1990)

ABSTRACT

The authors present their results concerning the thermal stability and nonisothermal decomposition kinetics of two coordination compounds with the general formula $[M(acac)_2(4Bzpy)_2]$, where M = Ni, Co; Hacac = acetylacetone; acac = the anion of Hacac; and 4Bzpy = 4-benzoylpyridine.

INTRODUCTION

Following our investigations into the thermal stability and nonisothermal decomposition kinetics of coordination compounds [1], this note deals with two coordination compounds with the chromophore MO_4N_2 in the trans configuration, as shown by the formula



$M = Co^{II}, Ni^{II}$

0040-6031/91/$03.50

EXPERIMENTAL

To synthesize the coordination compounds, the metal acetates were dissolved in ethanol. On adding the stoichiometric amount of acetylacetone in a solution of sodium acetate and keeping the system in a boiling-water bath, the metal acetylacetonates were precipitated. After collection by filtration, washing and drying, these solid intermediate compounds were treated with 4-benzoylpyridine in toluene medium. The obtained precipitates were subsequently washed with toluene and dried. In this way, crystalline powders (green in colour for the nickel compound and orange for the cobalt compound) were obtained.

The crystalline state of the coordination compounds, as well as the mean crystallite size, were determined with the aid of a Philips PW 1140 X-ray diffractometer using chromium K_α radiation. To calculate the mean crystallite sizes, Scherrer's formula [2] was applied.

The heating curves of the powders in the temperature range 20–1000 °C were obtained by using a MOM Budapest Q-1500 D Paulik–Paulik–Erdey type derivatograph with various heating rates between 1.38 and 13.1 K min^{-1}. The samples were heated in a static air atmosphere.

To evaluate the nonisothermal kinetic parameters of decomposition, the Coats–Redfern [3], Flynn–Wall at constant heating rate [4], Doyle–Gorbachev [5] and modified Coats–Redfern [6] integral methods were applied.

The experimental data were evaluated automatically using a program written in BASIC [7]. The same program allowed generation of the (α, t) curves (t in °C) using the values of the nonisothermal kinetic parameters and examination as to whether the experimental points lie on these curves.

RESULTS AND DISCUSSIONS

The values of the mean crystallite sizes, l, are

- for $[Ni(acac)_2(4Bzpy)_2]$ $l = 194$ Å
- for $[Co(acac)_2(4Bzpy)_2]$ $l = 140$ Å

The decomposition of $[Ni(acac)_2(4Bzpy)_2]$

According to the derivatographic data, the following reactions occur on progressive heating of the crystalline powder of $[Ni(acac)_2(4Bzpy)_2]$ at 10 K min^{-1}

$$[Ni(acac)_2(4Bzpy)_2](s) \xrightarrow{244\,^\circ C} Ni(acac)_2(4Bzpy)(s) + 4Bzpy(g) \; * \qquad (1a)$$

* The temperatures above the arrows, considered as reaction temperatures, correspond to the maximum decomposition rates on the peaks of the DTG curves at $\beta = 10$ K min^{-1}.

The solid product of the reaction, an unstable intermediate probably containing pentacoordinate nickel, undergoes the reaction at higher temperature

$$Ni(acac)_2(4Bzpy)(s) \xrightarrow{273\,^\circ C} Ni(acac)_2(s) + 4Bzpy(g) \quad (2a)$$

For this reaction the solid product should be actually formulated as $Ni_3(acac)_6$. As the electronic spectrum does not allow the clear identification of such a compound, and the X-ray diffractogram shows an amorphous compound, it seems probable that the trimeric structure is defective owing to traces of unevolved ligand or its degradation products.

The reaction undergone by $Ni(acac)_2(s)$ is

$$Ni(acac)_2(s) \xrightarrow{372\,^\circ C} \{Ni(acac)\}(s) + \{acac\}(g) \quad (3a)$$

The unstable reaction product decomposes according to the reaction

$$\{Ni(acac)\}(s) \xrightarrow{420\,^\circ C} NiO(s) + \{acac\}(g) \quad (4a)$$

Steps (3a) and (4a) are characterized by equal heights on the TG curve.

As far as the kinetic analysis is concerned, the only workable steps are (1a), (2a) and (4a). The values of the nonisothermal kinetic parameters for the steps are given, respectively, in Tables 1, 2 and 3.

TABLE 1

Values of the nonisothermal kinetic parameters for reaction (1a)

Kinetic parameters	Method			
	Coats–Redfern	Flynn–Wall β = const.	Doyle–Gorbachev	Modified Coats–Redfern
Heating rate				
$\beta = 5.45$ K min^{-1}				
E (kcal mol^{-1})	44.07	43.73	44.07	44.92
A (s^{-1}) [a]	2.09×10^{17}	1.55×10^{17}	2.09×10^{17}	5.43×10^{17}
n	1.1	1.1	1.1	1.1
r [b]	−0.9971	−0.9974	−0.9972	−0.9979
$\beta = 2.68$ K min^{-1}				
E (kcal mol^{-1})	43.90	43.56	43.90	42.27
A (s^{-1})	1.63×10^{17}	1.21×10^{17}	1.63×10^{17}	2.93×10^{16}
n	0.5	0.5	0.5	0.4
r	−0.9994	−0.9994	−0.9994	−0.9994
$\beta = 1.44$ K min^{-1}				
E (kcal mol^{-1})	38.42	38.25	38.42	37.96
A (s^{-1})	1.73×10^{15}	1.48×10^{15}	1.73×10^{15}	1.09×10^{15}
n	0	0	0	0
r	−0.9950	−0.9954	−0.9950	−0.9953

[a] A = preexponential factor.

[b] r is the correlation coefficient of the linear regression.

TABLE 2

Values of the nonisothermal kinetic parameters for reaction (2a)

Kinetic parameters	Method			
	Coats–Redfern	Flynn–Wall β = const.	Doyle–Gorbachev	Modified Coats–Redfern
Heating rate $\beta = 10.69$ K min^{-1}				
E (kcal mol^{-1})	95.07	92.42	95.07	95.25
A (s^{-1})	4.58×10^{36}	9.25×10^{35}	4.59×10^{36}	5.46×10^{36}
n	2.7	2.7	2.7	2.5
r	−0.9999	−0.9999	−0.9999	−0.9999
$\beta = 5.45$ K min^{-1}				
E (kcal mol^{-1})	89.93	97.47	89.93	86.71
A (s^{-1})	1.31×10^{36}	8.73×10^{34}	4.13×10^{35}	1.74×10^{34}
n	2.2	2.2	2.2	2.0
r	−0.9938	−0.9941	−0.9938	−0.9934

As may be seen from the inspection of the tables, the values of the nonisothermal kinetic parameters corresponding to reaction (1a) obtained by means of the four methods agree satisfactorily. A change of the kinetic parameters with the heating rate can also be noted. This could be assigned to the same heat transfer limitations; thus, the most reliable values of the kinetic parameters correspond to the lower heating rate value.

As far as reaction (2a) is concerned, relatively little dependence of the nonisothermal kinetic parameter values on the heating rate can be noted. Equally, one may note the high values of the activation energy and preex-

TABLE 3

Values of the nonisothermal parameters for reaction (4a)

Kinetic parameters	Method			
	Coats–Redfern	Flynn–Wall β = const.	Doyle–Gorbachev	Modified Coats–Redfern
Heating rate $\beta = 13.10$ K min^{-1}				
E (kcal mol^{-1})	68.75	67.95	68.75	66.01
A (s^{-1})	1.02×10^{20}	6.24×10^{19}	1.02×10^{20}	1.29×10^{19}
n	1.5	1.5	1.5	1.3
r	−0.9960	−0.9960	−0.9960	−0.9990
$\beta = 2.78$ K min^{-1}				
E (kcal mol^{-1})	100.89	98.35	100.89	101.45
A (s^{-1})	2.57×10^{31}	6.59×10^{30}	2.57×10^{31}	4.10×10^{31}
n	1.6	1.6	1.6	1.5
r	−0.9981	−0.9982	−0.9981	−0.9981

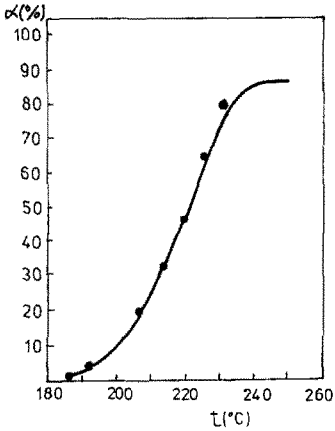


Fig. 1. Regenerated (α, t °C) curve for reaction (1a) at $\beta = 5.45$ K min^{-1}: (———) calculated curve with the values of Coats–Redfern parameters; (●) experimental points.

ponential factor as well as values of the reaction order > 2. The last fact supports the previously mentioned idea concerning the decomposition of a trimer.

Concerning reaction (4a), the differences between the activation energy and preexponential factor values for the two applied heating rates seem to compensate one another, giving practically the same decomposition rate.

The regenerated (α, t) curve (t in °C) for reaction (1a) at $\beta = 5.45$ K min^{-1} is given in Fig. 1. As is seen from the figure, the experimental points lie practically on the curve (which was based on the Coats–Redfern temperature integral).

The decomposition of $Co(acac)_2(4Bzpy)_2$

The decomposition steps recorded for the progressive heating of this compound are quite similar to the corresponding decomposition steps of the nickel compound. The representative chemical equations are

$$[Co(acac)_2(4Bzpy)_2](s) \xrightarrow{202\,^\circ C} Co(acac)_2 4Bzpy(s) + 4Bzpy(g) \quad (1b)$$

$$Co(acac)_2 4Bzpy(s) \xrightarrow{250\,^\circ C} Co(acac)_2(s) + 4Bzpy(g) \quad (2b)$$

$$Co(acac)_2 \xrightarrow{336\,^\circ C} \{Co(acac)\}(s) + \{acac\}(g) \quad (3b)$$

$$3Co\{(acac)\} \xrightarrow{480\,^\circ C} Co_3O_4(s) + 3\{acac\}(g) \quad (4b)$$

The difference with respect to the nickel compound lies in the final product of decomposition, which is Co_3O_4.

As far as the values of the nonisothermal kinetic parameters of decomposition are concerned, the only workable steps are (1b), (2b) and (4b). The

TABLE 4

Values of the nonisothermal kinetic parameters for reaction 1b

Kinetic parameters	Method			
	Coats–Redfern	Flynn–Wall β-const.	Doyle–Gorbachev	Modified Coats–Redfern
Heating rate $\beta = 9.14$ K min^{-1}				
E (kcal mol^{-1})	38.86	35.72	38.86	36.08
A (s^{-1})	8.01×10^{14}	2.28×10^{14}	5.04×10^{14}	3.40×10^{14}
n	1.6	1.6	1.6	1.5
r	−0.9968	−0.9971	−0.9968	−0.9978
$\beta = 5.37$ K min^{-1}				
E (kcal mol^{-1})	40.41	40.22	40.41	37.74
A (s^{-1})	2.02×10^{16}	1.72×10^{16}	2.03×10^{16}	1.10×10^{15}
n	1.3	1.3	1.3	1.1
r	−0.9958	−0.9962	−0.9958	−0.9961
$\beta = 2.20$ K min^{-1}				
E (kcal mol^{-1})	31.84	32.01	31.84	
A (s^{-1})	1.49×10^{12}	1.9×10^{12}	1.50×10^{12}	
n	0.2	0.2	0.2	
r	−0.9996	−0.9996	−0.9996	
$\beta = 1.38$ K min^{-1}				
E (kcal mol^{-1})	28.53	28.83	28.53	28.51
A (s^{-1})	4.83×10^{10}	7.34×10^{10}	4.90×10^{10}	5.03×10^{10}
n	0	0	0	0
r	−0.9872	−0.9886	−0.9872	−0.9886

TABLE 5

Values of the nonisothermal kinetic parameters for reaction (2b)

Kinetic parameter	Method			
	Coats–Redfern	Flynn–Wall β-const.	Doyle–Gorbachev	Modified Coats–Redfern
Heating rate $\beta = 9.14$ K min^{-1}				
E (kcal mol^{-1})	70.43	68.90	70.43	69.91
A (s^{-1})	6.65×10^{26}	2.20×10^{26}	6.66×10^{26}	3.98×10^{26}
n	1.5	1.5	1.5	1.4
r	−0.9933	−0.9936	−0.9933	−0.9922
$\beta = 5.36$ K min^{-1}				
E (kcal mol^{-1})	109.74	103.47	199.74	104.36
A (s^{-1})	1.51×10^{45}	1.12×10^{45}	1.51×10^{45}	5.44×10^{44}
n	1.5	1.4	1.5	1.1
r	−0.9993	−0.9993	−0.9993	−0.9991
$\beta = 2.79$ K min^{-1}				
E (kcal mol^{-1})	59.33	58.24	57.32	57.3
A (s^{-1})	1.07×10^{24}	4.46×10^{23}	1.07×10^{24}	1.93×10^{23}
n	1.5	1.5	1.5	1.3
r	−0.9945	−0.9948	−0.9945	−0.9943

TABLE 6

Values of the nonisothermal kinetic parameters for reaction (4b)

Kinetic parameters	Method			
	Coats–Redfern	Flynn–Wall β = const.	Doyle–Gorbachev	Modified Coats–Redfern
Heating rate $\beta = 9.93$ K min^{-1}				
E (kcal mol^{-1})	46.11	46.54	46.11	46.50
A (s^{-1})	2.44×10^{11}	3.81×10^{11}	2.45×10^{11}	3.42×10^{11}
n	1.6	1.6	1.6	1.6
r	−0.9990	−0.9991	−0.9990	−0.9991
$\beta = 2.76$ K min^{-1}				
E (kcal mol^{-1}	54.02	52.80	54.02	54.13
A (s^{-1})	4×10^{16}	3.5×10^{16}	4×10^{16}	6.82×10^{16}
n	1.9	1.9	1.9	1.9
r	−0.9990	−0.9990	−0.9990	−0.9990

respective values of the nonisothermal kinetic parameters are listed in Tables 4, 5 and 6.

The comments concerning these data are quite similar to the corresponding comments for reactions (1a), (2a) and (4a).

The regenerated (α, t) curve (t in °C) for reaction (1b) at $\beta = 5.37$ K min^{-1} is given in Fig. 2. As may be seen from the figure, the experimental points lie practically on the curve.

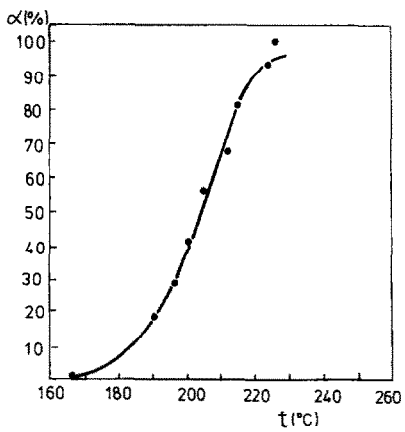


Fig. 2. Regenerated (α, t °C) curve for reaction (1b) at $\beta = 5.37$ K min^{-1}: (———) calculated curve with values of Coats–Redfern parameters; (●) experimental points.

CONCLUSIONS

1. An investigation of the thermal stability of the compounds $[Ni(acac)_2(4Bzpy)_2]$ and $[Co(acac)_2(4Bzpy)_2]$ was performed.

2. The nonisothermal kinetic parameter values for three decomposition steps and various heating rates were determined.

3. The values of the nonisothermal kinetic parameters obtained by means of four methods agree satisfactorily.

REFERENCES

1 (a) E. Segal and D. Fătu, Introduction to Nonisothermal Kinetics Editura Academiei RSR, Bucharest, 1983 (in Romanian). (b) D. Teică, E. Segal and M. Andruh, Thermochim. Acta, 178 (1991) 249.
2 A. Guinier, Theorie et Technique de la Radiocrystalographie, Dunod, Paris, 1964, p. 420.
3 A.W. Coats and J.P. Redfern, Nature (London), 201 (1964) 68.
4 J.H. Flynn and L.A. Wall, Polym. Lett., 4 (1966) 323.
5 (a) G.D. Doyle, Nature (London), 207 (1965) 290. (b) V.M. Gorbachev, J. Therm. Anal., 8 (1975) 349.
6 E. Urbanovici and E. Segal, Thermochim. Acta, 81 (1984) 379.
7 N. Dragoe and E. Segal, Thermochim Acta, in press.