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ON THE THERMAL DECOMPOSITION OF SOME COORDINATION COMPOUNDS OF COPPER(II) WITH BENZOYLPYRIDINE

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ABSTRACT

The authors present the results of a derivatographic investigation concerning the thermal stability of some coordination compounds with the formula $Cu(4Bzpy)_yX_2$ where $y = 2$ for $X = NO_3^-$ and $y = 1$ for $X = CH_3COO^-$.

INTRODUCTION

Following our research concerning thermal behaviour and nonisothermal decomposition kinetics of coordination compounds [1], we present in this paper our results concerning the thermal stability of $Cu(4Bzpy)(CH_3COO)_2$ and $Cu(4Bzpy)_2(NO_3)_2$ (4Bzpy = 4-benzoylpyridine).

EXPERIMENTAL

Powders of the above mentioned compounds were synthesized and analyzed according to the method described elsewhere [2]. The thermal curves (TG, DTG, DTA and T) were recorded by means of a derivatograph, MOM Budapest Q 1500 D, Paulik–Paulik–Erdey type, in a static air atmosphere at various heating rates in the range 0.6–10 K min^{-1} between 20 °C and 1000 °C.

The crystalline state of the powders was examined by use of an X-ray diffractometer (Philips PW 1140) using Cr K_α radiation. The mean crystallite sizes were calculated with the help of Scherrer's formula [3].

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The derivatographic data were used to evaluate the decomposition nonisothermal kinetic parameters by three methods, those of Coats–Redfern [4], Flynn–Wall for constant heating rate [5] and Coats–Redfern as modified by Urbanovici and Segal [6]. The experimental data were automatically processed using a program written in BASIC [7] which was run on a TIM S computer. The same program allowed regeneration of the thermogravimetric curves in the coordinates (α, t) using the values of the nonisothermal kinetic parameters and fitting them to the experimental points. For the regeneration of the TG curves in the above mentioned coordinates, the Coats–Redfern and Flynn–Wall values of the nonisothermal kinetic parameters were used.

RESULTS AND DISCUSSION

The decomposition of Cu(4Bzpy)(CH$_3$COO)$_2$

Powders of Cu(4Bzpy)(CH$_3$COO)$_2$ with the interplanar distances and mean crystallite size corresponding to the most intense line given in Table 1 were submitted to decomposition. According to the derivatographic data, the thermal decomposition occurs through the reactions described by the equations

$$\mathrm{Cu(4Bzpy)(CH_3COO)_2(s)} \xrightarrow{215\,^{\circ}\mathrm{C}} \mathrm{Cu(CH_3COO)_2(s) + 4Bzpy(g)}\ ^{*} \qquad (1)$$

$$\mathrm{Cu(CH_3COO)_2(s) + 4O_2(g)} \xrightarrow{385\,^{\circ}\mathrm{C}} \mathrm{CuO(s) + 4CO_2(g) + 3H_2O(g)} \qquad (2)$$

The copper oxide, as final solid product of decomposition for all the parent compounds used in this work, was identified by its X-ray diffractogram [8].

As far as the values of the nonisothermal kinetic parameters, reaction order, n, preexponential factor, A, and activation energy, E, are concerned, these are listed in Tables 2, 3 and 4 for reaction (1) and in Tables 5, 6 and 7 for reaction (2).

The inspection of Tables 2–4 shows a quite satisfactory agreement among the nonisothermal kinetic parameter values obtained by means of the three applied methods. From the same tables we can note a significant change in the values of the nonisothermal kinetic parameters with the heating rate. This could be assigned to heat transfer limitations at the higher rates.

Thus the most reliable results are those obtained at 1.57 K min^{-1}, the lowest heating rate used on this work. In such conditions the values of the nonisothermal kinetic parameters obtained at $\beta = 3.7$ K min^{-1}, which

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* The temperatures above the arrows correspond to the maximum decomposition rate (the peak of the DTG curve).

TABLE 1

Interplanar distances, *d*, relative intensities, I_{rel} and means crystallite size, *l*, for $Cu(4Bzpy)(CH_3COO)_2$

d (Å)	I_{rel}	*l* (Å)
14.13	100	255
9.24	32	–
9.01	30	–
7.05	32	–
5.58	72	–
4.05	43	–
3.71	22	–
3.66	19	–
3.12	53	–
3.09	61	–

TABLE 2

Values of nonisothermal kinetic parameters for reaction (1) at $\beta = 10.5$ K min^{-1}

	n	*A* (s^{-1})	*E* (kcal mol^{-1})	*r* [a]
Coats–Redfern	2.4	10^{17}	45.6	−0.99979
Flynn–Wall	2.4	10^{17}	45.3	−0.99981
Modified Coats–Redfern	2.5	16×10^{17}	47.9	−0.99987

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

TABLE 3

Values of nonisothermal kinetic parameters for reaction (1) at $\beta = 3.7$ K min^{-1}

	n	*A* (s^{-1})	*E* (kcal mol^{-1})	*r*
Coats–Redfern	1	1.01×10^{12}	33.0	−0.9993
Flynn–Wall	1	1.38×10^{12}	33.2	−0.9994
Modified Coats–Redfern	0.9	0.2×10^{12}	31.4	−0.9995

TABLE 4

Values of nonisothermal kinetics parameters for reaction (1) at $\beta = 1.57$ K min^{-1}

	n	*A* (s^{-1})	*E* (kcal mol^{-1})	*r*
Coats–Redfern	0.1	2.28×10^{4}	16.7	−0.9909
Flynn–Wall	0.1	1×10^{3}	17.7	−0.9927
Modified Coats–Redfern	0.1	1.58×10^{4}	16.2	−0.9928

TABLE 5

Values of nonisothermal kinetic parameters for reaction (2) at $\beta = 10.5$ K min^{-1}

	n	A (s^{-1})	E (kcal mol^{-1})	r
Coats–Redfern	2.1	3.9×10^{12}	48.4	−0.9987
Flynn–Wall	2.1	5.2×10^{12}	48.8	−0.9988
Modified Coats–Redfern	2.2	17.1×10^{12}	50.4	−0.9989

TABLE 6

Values of nonisothermal kinetic parameter for reaction (2) at $\beta = 3.7$ K min^{-1}

	n	A (s^{-1})	E (kcal mol^{-1})	r
Coats–Redfern	0.6	1.59×10^{6}	27.09	−0.9998
Flynn–Wall	0.6	5.3×10^{6}	28.2	−0.9991
Modified Coats–Redfern	0.6	1.7×10^{6}	27.0	−0.9993

TABLE 7

Values of nonisothermal kinetic parameters for reaction (2) at $\beta = 1.57$ K min^{-1}

	n	A (s^{-1})	E (kcal mol^{-1})	r
Coats–Redfern	0	1.76×10^{2}	15.72	−0.9971
Flynn–Wall	0	6.3×10^{2}	14.49	−0.9969
Modified Coats–Redfern	0	4.07×10^{2}	16.53	−0.9972

correspond to those predicted by the transition state theory [9], are quite surprising.

The regenerated TG curve for reaction (1) at $\beta = 3.7$ K min^{-1} on coordinates (α, t °C) is given in Fig. 1.

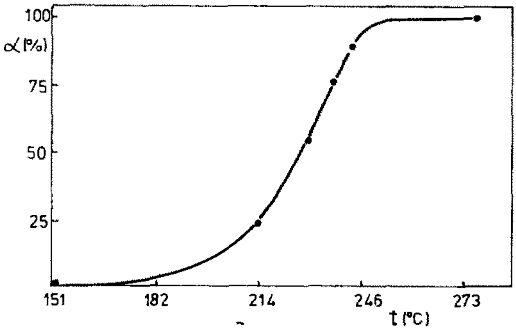

Fig. 1. Regenerated (α, t °C) curve for reaction (1) at $\beta = 3.7$ K min^{-1}: (———) calculated curve; (●) experimental points.

TABLE 8

Interplanar distances, d, relative intensities, I_{rel}, and mean crystallite size, l, for $Cu(4\text{-}Bzpy)_2(NO_3)_2$

d (Å)	I_{rel}	l (Å)
14.13	100	255
9.24	32	–
9.01	30	–
7.05	32	–
5.58	72	–
4.05	43	–
4.71	22	–
3.66	19	–
3.12	53	–
3.09	61	–

As is evident from the figure, the experimental points lie practically on the calculated curve; this shows the reliability of the method applied to evaluate the nonisothermal kinetic parameters, and also of the values determined.

As far as reaction (2) is concerned, Tables 5–7 show, as in the previous case, a change of the nonisothermal kinetic parameter values with the heating rate, thus showing heat transfer limitations.

One should note in this case also the value $n = 0.6$ at $\beta = 3.7$ K min^{-1}, quite close to the value corresponding to a contracting sphere model [10].

The decomposition of $Cu(4Bzpy)_2(NO_3)_2$

Table 8 shows the powder diffractometric data corresponding to this compound.

The derivatograms of this compound allow us to postulate the reaction

$$Cu(4Bzpy)_2(NO_3)_2(s) \xrightarrow{255°C} Cu(NO_3)_2(s) + 2(4Bzpy)(g) \qquad (3)$$

followed at higher temperatures by a decomposition in two stages to CuO. The only decomposition step suitable for the evaluation of the nonisothermal kinetic parameters is reaction (3).

The three applied methods lead to the values shown in Table 9.

TABLE 9

Values of nonisothermal kinetic parameters for reaction (3) at $\beta = 6.5$ K min^{-1}

	n	A (s^{-1})	E (kcal mol^{-1})	r
Coats–Redfern	1.2	6.15×10^{25}	71.06	−0.9981
Flynn–Wall	1.2	2.04×10^{27}	69.53	−0.9984
Modified Coats–Redfern	1.1	4.5×10^{26}	68.36	−0.9988

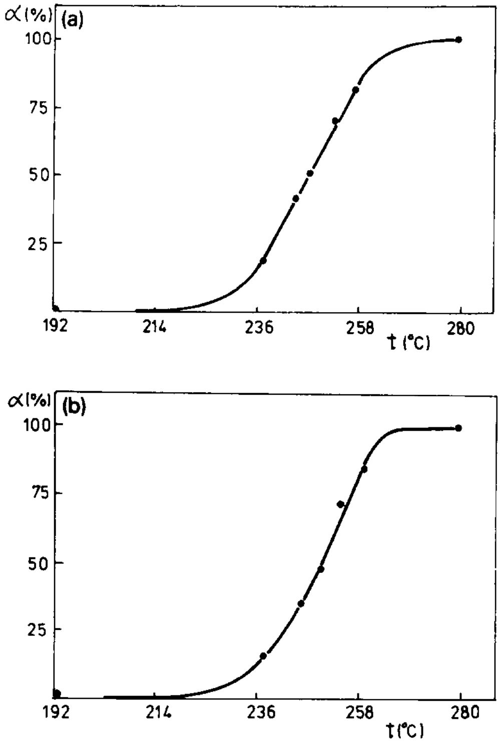

Fig. 2. Regenerated (α, t °C) curve for reaction (3) at $\beta = 6.5$ K min^{-1}: (———) calculated curve; (●) experimental points. (a) Nonisothermal kinetic parameter values determined by the Coats–Redfern method; (b) nonisothermal kinetic parameter values determined by the Flynn–Wall method.

The (α, t) curves regenerated using the values of the nonisothermal kinetic parameters determined according to the Coats–Redfern and Flynn–Wall methods are given in Fig. 2.

One can note in this case, too, a satisfactory agreement among the values of the nonisothermal kinetic parameter values obtained by the three applied methods. As far as the quite high values of the preexponential coefficient and activation energy are concerned, these lead to normal values of the specific rate (the high value of the preexponential factor is compensated by the correspondingly low value of the exponential factor on the Arrhenius equation).

CONCLUSIONS

1. The nonisothermal kinetic parameters of the thermal decomposition reactions undergone by Cu(4Bzpy)($CH_3COO)_2$ and Cu(4Bzpy$)_2(NO_3)_2$ have been determined.

2. The values of the nonisothermal kinetic parameters obtained by three methods are in satisfactory agreement.

3. A change of the nonisothermal kinetic parameter values with the heating rate was evident.

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