

KINETIC PARAMETERS OF THERMAL DECOMPOSITION OF NITROCUPRATES (II)

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(Received March 1, 1978; in revised form November 13, 1978)

Kinetic parameters of thermal decomposition of compounds of the general formula $M_2^I M^{II} [Cu(NO_2)_6]$ (where $M^I = K^+, Rb^+$ or Cs^+ ; and $M^{II} = Ca^{2+}, Sr^{2+}, Ba^{2+}$ or Pb^{2+}) and $K_2Pb[X(NO_2)_6]$ (where $X = Co^{2+}, Ni^{2+}, Zn^{2+}$) are determined from the corresponding thermal curves. The order of reaction (n) and the activation energy (E_a) are derived. The kinetic data is discussed in terms of the effects of outer sphere cations and the central ion on the activation energy.

A method for nitritocuprate preparation and the mechanism of their thermal decomposition is given in a previous paper [1]. This paper describes calculations of the order of reaction and the activation energy of these reactions. The values are determined using Coats and Redfern's method [2] and Doyle's method modified by Zsakó [3]. The object of the present work was to examine the effect of outer sphere cations on the activation energy of thermal decomposition of nitritocuprates (II). Kinetic parameters of the decomposition of complex salts of the general formula $K_2Pb[X(NO_2)_6]$ (where $X = Co^{2+}, Ni^{2+}, Zn^{2+}$) were also determined in order to investigate the effect of the central ion on the activation energy.

Experimental

Determination of kinetic parameters

Coats and Redfern's method

Coats and Redfern [2] proposed a method to determine the order of reaction on the basis of thermogravimetric data, based on a plot of $\log \left(\frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right) = A$ against $\frac{1}{T} \cdot 10^3$.

Where: α – thermal decomposition rate of the sample, calculated from the TG curve, from the formula $\alpha = \frac{W_0 - W}{W_0 - W_k}$; in which W_0, W_k

and W are initial weight, final weight and the weight of the sample at the temperature T

n – order of reaction

T – temperature (K).

A number of such relationships are plotted for a number of assumed values of n . The correct value of n for a given thermal decomposition reaction, gives a straight line. The activation energy is calculated from the equation:

$$E = 2.3 \cdot R \operatorname{tg} \beta$$

where: $\operatorname{tg} \beta$ – the slope of the straight line found in the previous plot

R – gas constant.

Fig. 1 shows the plots of the above discussed relationship for $\text{K}_2\text{Sr}[\text{Cu}(\text{NO}_2)_6]$ for $n = 0.5, 1.0$ and 2.0 .

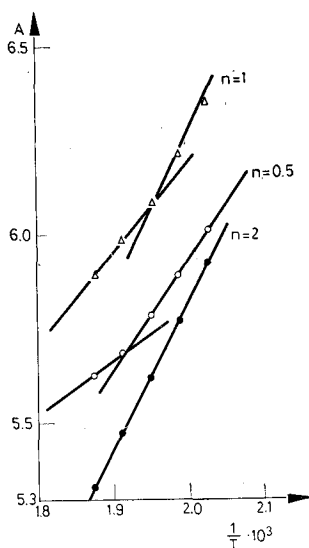


Fig. 1. Graphic determination of the order of reaction. $A = -\log \left[\frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right]$ for $n = 0.5$ and 2.0 and $-\log \left[\frac{-\log(1 - \alpha)}{T^2} \right]$ for $n = 1$

Orders of reaction, determined in this way, had the same value – 2 – for all the examined compounds.

Table 1 gives values of the activation energy for the thermal decomposition of the investigated compounds, calculated by Coats and Redfern's method.

Table 1

The values of the activation energy of thermal decomposition of the tested salts

| No | Compound formula | E_a , kcal/mole |
|----|----------------------|----------------------|
| 1 | $K_2Ca[Cu(NO_2)_6]$ | 13.15 |
| 2 | $Rb_2Ca[Cu(NO_2)_6]$ | 37.61 |
| 3 | $Cs_2Ca[Cu(NO_2)_6]$ | 43.14 |
| 4 | $K_2Sr[Cu(NO_2)_6]$ | 17.78 |
| 5 | $Rb_2Sr[Cu(NO_2)_6]$ | 47.23 |
| 6 | $Cs_2Sr[Cu(NO_2)_6]$ | 51.66 |
| 7 | $K_2Ba[Cu(NO_2)_6]$ | 19.80 |
| 8 | $Rb_2Ba[Cu(NO_2)_6]$ | 36.26 |
| 9 | $Cs_2Ba[Cu(NO_2)_6]$ | 46.49 |
| 10 | $K_2Pb[Cu(NO_2)_6]$ | 27.18 |
| 11 | $Rb_2Pb[Cu(NO_2)_6]$ | 32.67 |
| 12 | $Cs_2Pb[Cu(NO_2)_6]$ | 46.59 |
| 13 | $K_2Pb[Ni(NO_2)_6]$ | 37.72 |
| 14 | $K_2Pb[Co(NO_2)_6]$ | 35.65 |
| 15 | $K_2Pb[Zn(NO_2)_6]$ | 22.98 |

Doyle's method, modified by Zsakó

The order of reaction and the activation energy of nitrocuprates of the general formula $M_2Sr[Cu(NO_2)_6]$ (where $M^I = K^+, Rb^+, Cs^+$) were calculated on the basis of the same thermogravimetric data, using Doyle's method modified by Zsakó. Doyle formulated the following equation of the thermogravimetric curve

$$g(\alpha) = \frac{Z \cdot E_a}{R \cdot q} p(x)$$

where: $g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}$ and $f(\alpha)$ is a certain function of the initial compound reacted

E_a — activation energy

Z — pre-exponential factor

q — heating rate

$p(x)$ — the function of temperature and activation energy.

Zsakó gave Doyle's equation in a logarithmic form:

$$\log \frac{Z \cdot E_a}{R \cdot q} = \log g(\alpha) - \log p(x) = B$$

$g(\alpha)$ can be calculated for different temperatures and for known $f(\alpha)$, on the basis of the thermogravimetric data. $p(x)$ for assumed activation energy can be found for the same temperatures. The activation energy is selected by a trial-and-error method. For a given thermal decomposition such a value of E_a is accepted for which B has the least temperature variation. The variation is characterized by a standard deviation (δ) of individual B values from the arithmetic mean \bar{B} .

$$\delta = \sqrt{\frac{(B - \bar{B})^2}{r}}$$

where: r – the number of individual values of B . The minimum value of δ indicates the accepted value of the activation energy. The least value of δ also indicates the correlation of thermal decomposition and a given $f(\alpha)$ for different assumed $f(\alpha)$.

The simplest equation of thermal decomposition of solids is:

$$f(\alpha) = (1 - \alpha)^n$$

where: n – order of reaction.

Function $g(\alpha)$ was calculated for the order of reaction using the following equation:

$$g(\alpha) = \frac{\alpha}{1 - \alpha}$$

α – thermal decomposition rate of the investigated compounds, calculated in the same way as in Coats and Redfern's method. The values of $\log p(x)$ for the investigated temperature range and for different values of the activation energy were taken from the tables [3].

By use of the above-mentioned calculation method we obtained the values of the activation energy presented in Table 2.

Table 2

The values of the activation energy and of the standard deviation

| No | Compound formula | E_a , kcal/mole | δ |
|----|----------------------|----------------------|----------|
| 1 | $K_2Sr[Cu(NO_2)_6]$ | 17.9 | 0.0030 |
| | | 18.0 | 0.0027 |
| | | 18.1 | 0.0028 |
| 2 | $Rb_2Sr[Cu(NO_2)_6]$ | 46.7 | 0.0158 |
| | | 46.8 | 0.0157 |
| | | 46.9 | 0.0158 |
| 3 | $Cs_2Sr[Cu(NO_2)_6]$ | 51.8 | 0.0003 |
| | | 51.9 | 0.0001 |
| | | 52.0 | 0.0007 |

Table 3 contains the values of the activation energy of $M_2^I Sr[Cu(NO_2)_6]$ calculated by Coats and Redfern's method and by Zsakó's method.

Table 3

The comparison of the values of the activation energy, determined by Coats and Redfern's method and by Zsakó's one

| No | Compound formula | Activation energy, kcal/mole | |
|----|----------------------|------------------------------|----------------|
| | | Redfern's method | Zsakó's method |
| 1 | $K_2Sr[Cu(NO_2)_6]$ | 17.78 | 18.0 |
| 2 | $Rb_2Sr[Cu(NO_2)_6]$ | 47.23 | 46.8 |
| 3 | $Cs_2Sr[Cu(NO_2)_6]$ | 51.66 | 51.9 |

Discussion

The investigations prove that the order of reaction of the decomposition of all examined salts is 2. The activation energy varies from 13 kcal/mole up to 50 kcal/mole. The activation energy increases and decreases together with increase and decrease of the temperature of the first endothermic peaks [1]. The activation energy of decomposition of nitritocuprates depends on outer sphere cations and increases together with the increase of M^I ionic cation radius. The relationship between the activation energy and the difference of ionic radii $2r_{M^I} - r_{M^{II}}$ is shown in Fig. 2. Caesium salts have the highest activation energy, the lowest

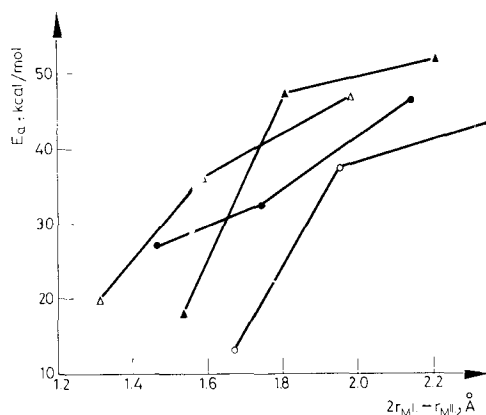
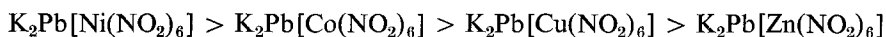


Fig. 2. Dependence of the activation energy on the thermal decomposition of nitritocuprates on the difference in the radii of outer sphere cations. The change of M^I cation.
 ○ M^I Ca $[Cu(NO_2)_6]$; ▲ M_2^I Sr $[Cu(NO_2)_6]$; △ M_2^I Ba $[Cu(NO_2)_6]$; ● M_2^I Pb $[Cu(NO_2)_6]$

values were obtained for potassium salts. The high activation energy of thermal decomposition of nitritocuprates of rubidium and caesium, as different from potassium, may be explained on the basis of their structure, when carrying out calculations of the distance between the complex anions and outer surface of potassium group ions [1].

In the case of the same M^I cation, and change of M^{II} cation, the highest values of activation energy are obtained for strontium salts. Salts of calcium, barium and lead have similar values.

The comparison of the values of the activation energy of complex nitrite salts, containing different central ions and the same outer sphere cations, proves that the salts can be graded according to the decreasing values of the activation energy:



Nickel salt is the most stable one. It has the highest stabilization energy of the crystalline field. In cases of octahedral high-spin complexes it is (in Dq) 12 Dq for nickel, 6 Dq for copper and 0 Dq for zinc. The salt $K_2Pb[Co(NO_2)_6]$ is a low-spin complex, with one electron in the 4 d orbital [4].

References

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RÉSUMÉ — Les paramètres cinétiques de la décomposition thermique des composés de formule générale $M_2^I M^{II} [Cu(NO_2)_6]$ où $M^I = K^+, Rb^+$ ou Cs^+ et $M^{II} = Ca^{2+}, Sr^{2+}, Ba^{2+}$ ou Pb^{2+} et $K_2Pb[X(NO_2)_6]$ où $X = Co^{2+}, Ni^{2+}, Zn^{2+}$ ont été déterminés à partir des courbes thermo-analytiques correspondantes. L'ordre de réaction (n) et l'énergie d'activation (E_a) ont été calculés. Les effets des cations de la sphère externe et ceux de l'ion central sur l'énergie d'activation sont discutés.

ZUSAMMENFASSUNG — Die kinetischen Parameter der thermischen Zersetzung von Verbindungen des allgemeinen Typs $M_2^I M^{II} [Cu(NO_2)_6]$ ($M^I = K^+, Rb^+$ oder Cs^+ ; $M^{II} = Ca^{2+}, Sr^{2+}, Ba^{2+}$ oder Pb^{2+}) bzw. $K_2Pb[X(NO_2)_6]$ ($X = Co^{2+}, Ni^{2+}, Zn^{2+}$) werden aus den entsprechenden thermischen Kurven bestimmt. Die Reaktionsordnung (n) und die Aktivierungsenergie (E_a) werden abgeleitet. Die kinetischen Parameter werden hinsichtlich der Effekte der Kationen in der äußeren Sphäre und des zentralen Ions auf die Aktivierungsenergie diskutiert.

Резюме — Из соответствующих термических кривых определены кинетические параметры термического разложения соединений общей формулы $M_2^I M^{II} [Cu(NO_2)_6]$, где $M^I = K^+, Rb^+$ или Cs^+ ; $M^{II} = Ca^{2+}, Sr^{2+}, Ba^{2+}$ или Pb^{2+} , а также соединений $K_2Pb[X(NO_2)_6]$, где $X = Co^{2+}, Ni^{2+}, Zn^{2+}$. Установлены порядок реакции (n) и энергия активации (E_a). Кинетические данные обсуждены на основе влияния внешнесферных катионов и центрального иона на энергию активации.