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KINETIC PARAMETERS OF THE THERMAL DECOMPOSITIONS OF NITRITONICKELATES(II)

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Kinetic parameters of thermal decomposition of compounds of general formula $M^{I}_{2}M^{II}[Ni(NO_2)_6]$, where $M^{I} = K^{+}$, Rb^{+} or Cs^{+} and $M^{II} = Ca^{2+}$, Sr^{2+} or Ba^{2+}, were investigated on the basis of the respective thermal curves. Calculations of the reaction order and activation energy carried out by the Coats-Redfern method and by Doyle's method (modified by Zsakó) gave similar results, The reaction order is 2 for all the compounds investigated. In the group of potassium salts the activation energy increases from $M^{II} = Ca^{2+}$ to $M^{II} = Ba^{2+}$. In the groups of rubidium and caesium salts, the lowest activation energy is observed when $M^{II} = Sr^{2+}$. Such behaviour of the nitritonickelates is explained in terms of structures and the principle of maximum density.

Nitritonickelates are crystalline salts with regular space networks. The methods used to obtain them, and the mechanism of their thermal decomposition, were described earlier [1]. In this paper we present calculations of the reaction order n and activation energy E_a of this decomposition. The calculations were carried out by Coats and Redfern's method [2], and by Doyle's method as modified by Zsakó [3].

Calculation of kinetic parameters

The reaction order was calculated according to Coats and Redfern's method. The calculation technique and equations used were given earlier [4].

Thermogravimetric data of $K_2Sr[Ni(NO_2)_6]$ were used to calculate the relationship between $A = -\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]$ and $\frac{1}{T}\cdot 10^3$ (Fig. 1), where $\alpha = \frac{w_0 - w}{w_0 - w_t}$ and w_0, w and w_t are the initial mass, final mass and mass of the sample at temperature T, respectively,

n = reaction order, T = temperature (K), n was assumed to be 0, 1 and 2. When $n = 1$ another equation was used: $A = -\log\left[\frac{-\log(1-\alpha)}{T^2}\right]$. The reaction order determined in this way was 2 for all compounds tested.

Doyle's method (Zsakó's modified version) was used to calculate the reaction order, the same thermogravimetric data being used. Standard deviations (δ) were

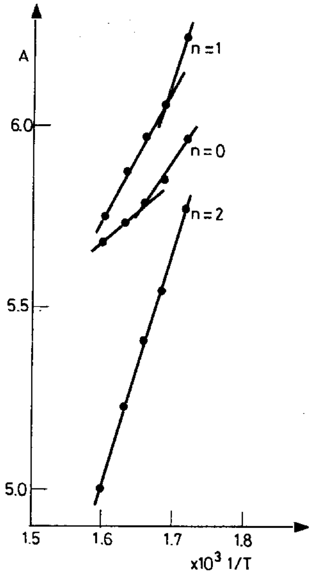

Fig. 1. Graphic determination of the order of reaction $A = -\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]$ for $n = 0$ and 2 and $-\log\left[\frac{-\log(1-\alpha)}{T^2}\right]$ for $n = 1$

calculated. The assumptions were $n = 0$, 1 and 2, the respective functions for $g(\alpha)$ being $g_0(\alpha) = \alpha$; $g_1(\alpha) = -\ln(1-\alpha)$; $g_2(\alpha) = \frac{\alpha}{1-\alpha}$.

The results are given in Table 1.

Table 2 gives values of the activation energy of thermal decomposition for the compounds under test as calculated by Coats and Redfern's method and by Zsakó's modified method.

Table 1

Values of minimum standard deviation (δ) calculated from thermogravimetric data for $K_2Sr[Ni(NO_2)_6]$

$n = 0$		$n = 1$		$n = 2$	
Ea, kJ/mole	Δ	Ea, kJ/mole	Δ	Ea, kJ/mole	Δ
117.2	0.1430	100.5	0.0626	117.2	0.0351
125.6	0.1162	108.8	0.0584	125.6	7.0264
134.0	0.1772	117.2	0.0744	134.0	0.0288

Table 2

Values of activation energy of thermal decomposition for salts under test

No	Compound formula	Activation energy	
		Redfern's method, kJmole^{-1}	Zsako's method, kJmole^{-1}
1	$K_2Ca[Ni(NO_2)_6]$	133.14	134.0
2	$K_2Sr[Ni(NO_2)_6]$	134.65	127.3
3	$K_2Ba[Ni(NO_2)_6]$	193.35	203.9
4	$Rb_2Ca[Ni(NO_2)_6]$	240.57	238.6
5	$Rb_2Sr[Ni(NO_2)_6]$	174.42	186.3
6	$Rb_2Ba[Ni(NO_2)_6]$	250.79	248.7
7	$Cs_2Ca[Ni(NO_2)_6]$	260.08	259.6
8	$Cs_2Sr[Ni(NO_2)_6]$	157.38	134.0
9	$Cs_2Ba[Ni(NO_2)_6]$	226.21	213.1

Discussion

The effect of outer sphere cations M^I and M^{II} in $M^I_2M^{II}[X(NO_2)_6]$ (where X is a central divalent metal) can be analyzed either by varying M^I while M^{II} remains the same, or by varying M^{II} while M^I remains the same. These two possibilities are discussed below:

Variation of M^I

In the case of the calcium group ($M^{II} = Ca^{2+}$) of nitritonickelates, the activation energy increased when the ionic radius of M^I was increased. The potassium salt was the least stable; the greatest stability was shown by the caesium salt. This is in agreement with what was found earlier [4] for nitritocuprates of all groups. The change in activation energy is not regular for this group (nor for the other groups either). (Fig. 2).

The difference between the activation energies of potassium-calcium nitritonickelate and rubidium-calcium nitritonickelate is 107.4 kJ/mole; whereas in the case of the rubidium-calcium salt and the caesium-calcium salt the difference is only 19.5 kJ/mole. The changes in activation energy for the salts of the strontium and barium groups are different from the changes in the case of the calcium group. The greatest activation energy is shown by the rubidium salt. The differences between the activation energies of the rubidium and caesium salts, however, are not considerable (about 20.9 kJ/mole).

As far as the decomposition temperatures are concerned, the potassium salts are less stable than the rubidium and caesium salts. The rubidium and caesium salts, however, decompose at nearly the same temperatures (Fig. 3).

Thus, the stability of a compound can be considered as characteristic of the activation energy. The different behaviour of the various nitritonickelate groups

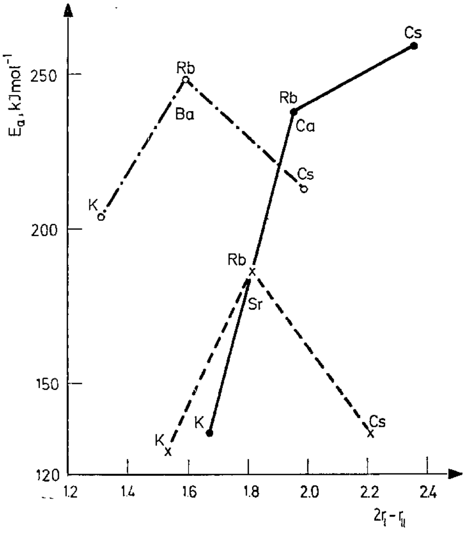

Fig. 2. Dependence of the activation energy on the thermal decomposition of nitritonickelates(II) on the difference in the radii of outer sphere cations. Change of M^I cation.
● M^I_2Ca[Ni(NO$_2$)$_6$]; × M^I_2Sr[Ni(NO$_2$)$_6$]; ○ M^I_2Ba[Ni(NO$_2$)$_6$]

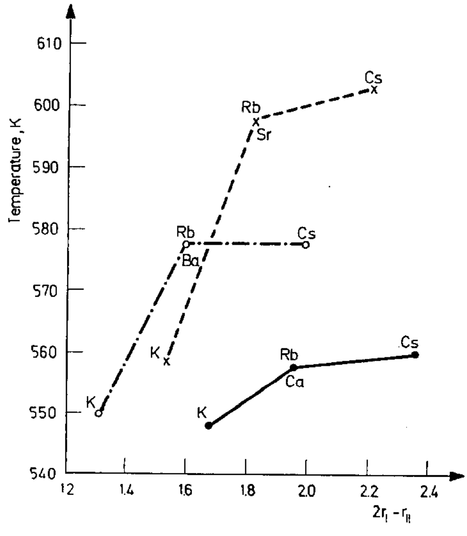

Fig. 3. The dependence of thermal decomposition temperatures for nitritonickelates(II) on the difference of radii of outer sphere cations. Change of M^I cation
● M^I_2Ca[Ni(NO$_2$)$_6$]; × M^I_2Sr[Ni(NO$_2$)$_6$]; ○ M^I_2Ba[Ni(NO$_2$)$_6$]

can have structural causes and can be explained in terms of the principle of densest packing. X-ray investigations proved that nitritonickelates belonging to the same group, as well as nitritonickelates of different groups, are isostructural. Space gaps with M^I and M^{II} cations are filled more densely for the caesium-calcium salts than for the potassium-calcium and rubidium-calcium salts. In the cases of the strontium and barium groups, the gaps are filled most densely earlier than for the rubidium salts; therefore, they are the stablest salts. This is conditioned by the longer ionic radii of strontium and barium.

Variation of M^{II}

The change in activation energy of nitritonickelates accompanying the variation of M^{II} in the different groups has several variants. In the potassium group ($M^I = K^+$) the activation energies of the calcium and strontium salts are very similar. The greatest activation energy is shown by the barium salt. The sequence of changes in activation energy is the same as for the nitritocuprates of the potassium group.

The lowest activation energies occur for the strontium salt in the cases of the rubidium and caesium groups. Differences in activation energy for salts of a given group are considerable – about 62.8 kJ/mol. The relationship is the reverse in comparison with the nitritocuprates of the rubidium and caesium groups, where the strontium salt showed the greatest activation energy. There is also a reverse relationship between the activation energies of nitritonickelates and the temperatures of thermal decomposition (Figs 4 and 5). The decomposition temperature is highest for the strontium salts – their highest stability can have a structural

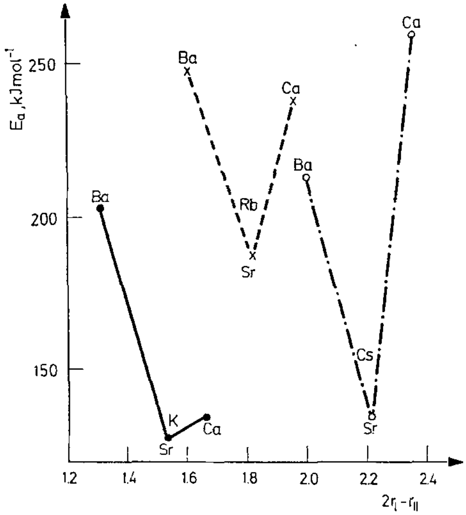

Fig. 4. Dependence of the activation energy on the thermal decomposition of nitritonickelates(II) on the difference in the radii of outer sphere cations. Change of M^{II} cation
● $K_2M^{II}[Ni(NO_2)_6]$; × $Rb_2M^{II}[Ni(NO_2)_6]$; ○ $Cs_2M^{II}[Ni(NO_2)_6]$

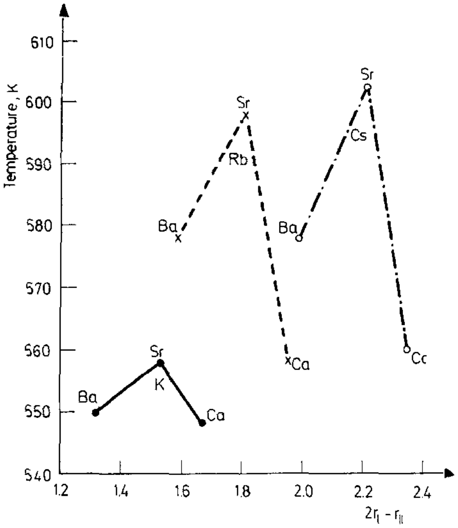

Fig. 5. The dependence of thermal decomposition temperatures for nitritonickelates(II) on the difference of radii of outer sphere cations. Change of M^{II} cation
● $K_2M^{II}[Ni(NO_2)_6]$; × $Rb_2M^{II}[Ni(NO_2)_6]$; ○ $Cs_2M^{II}[Ni(NO_2)_6]$

explanation on the principle of densest packing. The incompatibility between the activation energy and the temperature of thermal decomposition is characteristic of nitritonickelates. It should be stressed, however, that such an incompatibility has also been observed for some groups of other compounds; the examples are ammine complexes of cobalt(III), investigated by Wendlandt and Smith [5], where the decomposition temperatures and the activation energies were 86° an 19 kcal/mol (79.5 kJ/mole) for $[Co(NH_3)_5 \cdot H_2O]Cl_3$, 85° and 25 kcal/mole (104.7 kJ/mole) for $[Co(NH_3)_5 \cdot H_2O]Br_3$, and 82° and 31 kcal/mol (129.8 kJ/mol for $[Co(NH_3)_5 \cdot \cdot H_2O(NO_3)_3]$. Similar changes were observed for chromium(III) ammine complexes [5].

Changes in temperatures and in activation energies are also incompatible in some complexes with organic ligands, e.g. mercaptobenzothiazole complexes of bismuth(III) and nickel(II) [6]. Exceptionally large increases in activation energy, with small, but progressive corresponding decreases in thermal decomposition temperature were observed for mono-, di- and tri-methylammonium perchlorates [7] [319° an 14.4 kcal/mole (60.3 kJ/mole) for $CH_3NH_3ClO_4$, 312° and 57.2 kcal/mole (239.5 kJ/mole) for $(CH_3)_2NH_2ClO_4$, 305° and 79.6 kcal/mole (333.3 kJ/mole) for $(CH_3)_3NHClO_4$]. In the case of tetramethylammonium perchlorate the decomposition temperature was 422°, but the activation energy decreased down to 50.4 kcal/mole (211.0 kJ/mole). The explanation of why the incompatibility between changes in decomposition temperatures and changes in activation energy occurs for some groups of compounds should be the subject of future investigations, carried out to provide further series of experimental data.

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ZUSAMMENFASSUNG — Die kinetischen Parameter der thermischen Zersetzung von Verbindungen der allgemeinen Formel $M_2^IM^{II}[Ni(NO_2)_6]$ ($M^I = K^+$, Rb^+ oder Cs^+ und $M^{II} = Ca^{2+}$, Sr^{2+} oder Ba^{2+}) wurden auf Grund der entsprechenden thermischen Kurven untersucht. Die an Hand der Coats-Redfern Methode und der durch Zsakó modifizierten Doyleschen Methode durchgeführten Berechnungen der Reaktionsordnung und der Aktivierungsenergie ergaben ähnliche Resultate. Die Reaktionsordnung ist 2 für sämtliche untersuchten Verbindungen. In der Gruppe der Kaliumsalze steigt die Aktivierungsenergie von $M^{II} = Ca^{2+}$ in Richtung $M^{II} = Ba^{2+}$ an. In der Gruppe der Rubidium- und Caesiumsalze wird die niedrigste Aktivierungsenergie bei $M^{II} = Sr^{2+}$ beobachtet. Dieses Verhalten der Nitritonickelate wird durch die Strukturen und das Prinzip der maximalen Dichte erklärt.

Резюме — На основе соответствующих термических кривых были исследованы кинетические параметры термического разложения соединений общей формулы $M_2^I M^{II}[Ni(NO_2)_6]$, где $M^I = K^+$, Rb^+ и Cs^+, а $M^{II} = Ca^{2+}$, Sr^{2+} и Ba^{2+}. Расчеты порядка реакции и энергии активации, проведенные по методу Коутса-Рэдферна и по методу Дойля (видоизмененный Жаком), дали совпадающие результаты. Для всех исследованных соединений порядок реакции составил 2. Для калиевых солей энергия активации увеличивается при переходе от Ca^+ до Ba^{2+}. В группе солей рубидия и цезия наиболее низкое значение энергии активации установлено для $M^{II} = Sr^{2+}$. Такое поведение нитритных солей никеля объяснено с точки зрения их структуры и принципа максимальной плотности.