# Synthesis and thermal investigations of K₂M(IO₃)₄ · 2H₂O where M²⁺ is Co²⁺, Ni²⁺, Zn²⁺. Part 1.

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**Abstract**

New methods were applied in the synthesis of double salt iodates of the type K₂M(IO₃)₄ · 2H₂O (where Me is Co²⁺, Ni²⁺, Zn²⁺). Their thermal and calorimetric behaviour were investigated by DTA, TG and DSC. Simultaneous dehydration and decomposition of the binary salt give simple iodites. Mixtures of KIO₃ and Me(IO₃)₂ were melted, followed by the latter's decomposition along familiar pathways. The $\Delta H^{\ominus}_{\text{ph.tr.}}$ values were recorded from the DSC curves, while the TG curves were processed by the methods of formal kinetics, and the kinetic parameters $E^*$ and $A$ calculated. The type of kinetic equation for the dehydration process was also determined.

INTRODUCTION

The information for obtaining the double salts of the K₂M(IO₃)₄ · 2H₂O type (where M²⁺ is Co²⁺, Ni²⁺, Zn²⁺, Mn²⁺) is derived from investigation of the ternary systems KIO₃–M(IO₃)₂–H₂O at 50°C [1–3]. The double salts were isolated under the conditions of equilibrium attained in the course of 30-day treatment and were identified by comparing their DTA and TG curves taken in the region of the dehydration process with those of the corresponding M(IO₃)₂ · 2H₂O. The greater stability of the double salts, compared to that M(IO₃)₂ · 2H₂O.

According to Cordfunke [4], upon mixing solutions of KIO₃ and Co(NO₃)₂ · 6H₂O under particular conditions a double salt of composition K₂Co(IO₃)₄ · 2H₂O was obtained instead of Co(IO₃)₂ · nH₂O.

The aim of this study is to determine the optimum conditions of synthesis of M₂ᴵMᴵᴵ(IO₃)₄ · 2H₂O (where Mᴵ is K⁺, and Mᴵᴵ = Co²⁺, Ni²⁺, Zn²⁺) from nonequilibrium systems and to study their thermal and calorimetric

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behaviour by DTA, TG and DSC. The aim is also, on the basis of the data obtained, to determine certain hydrodynamic and kinetic parameters of the dehydration process.

EXPERIMENTAL

$K_2M^{II}(IO_3)_4 \cdot 2H_2O$ salts were obtained by adding solid $M(IO_3)_2 \cdot 2H_2O$ (where $M^{2+} = Co^{2+}$, $Ni^{2+}$, $Zn^{2+}$) to saturated solution of $KIO_3$ at $T = 65°C$ with continuous stirring of the mixture using a magnetic agitator. The time for obtaining $K_2Zn(IO_3)_4 \cdot 2H_2O$ was 6 h, for $K_2Co(IO_3)_4 \cdot 2H_2O$ was 8 h, and for $K_2Ni(IO_3)_4 \cdot 2H_2O$ 12 h, i.e. the conditions of synthesis were most favourable for $K_2Zn(IO_3)_4 \cdot 2H_2O$. This is in accord with the hypothesis advanced by Balarev [5] on the positive influence of the zero value of the crystal field stabilization energy (CFSE) of $M^{2+}$ on double salt formation. The experimental data indicate that the respective anhydrous iodates can also be used as starting materials. In this case, however, the conditions for synthesis are considerably less favourable.

The compounds obtained and the intermediate phases have been identified by X-ray and quantitative analysis as follows: $Zn^{2+}$, $Co^{2+}$ and $Ni^{2+}$, complexometrically [6], $K^+$, by weight through precipitation with sodium tetraphenylborate [7]; iodine, iodometrically [8]; water, after Fisher's method and thermogravimetrically. The data are presented in Table 1.

The thermal investigations were carried out on a Paulik Erdey MOM-OD-102 derivatograph at a heating rate of $10°C \, min^{-1}$ to 900°C, while the calorimetric studies were made with a Perkin-Elmer DSC-4 apparatus in the 50–300°C region in standard pans. The kinetic analysis was made on the basis of TG curves taken at a heating rate of $5°C \, min^{-1}$ up to 500°C.

TABLE 1

Data from the quantitative analysis of $K_2M(IO_3)_4 \cdot 2H_2O$ (where $M^{2+}$ is $Co^{2+}$, $Ni^{2+}$, $Zn^{2+}$)

| Compound | $K^+$ in % | | $M^{2+}$ in % | | $IO_3^-$ in % | | $H_2O$ in % | |
|---|---|---|---|---|---|---|---|---|
| | Theor. | Exp. | Theor. | Exp. | Theor. | Exp. | Theor. | Exp. |
| $K_2Co(IO_3)_4 \cdot 2H_2O$ | 8.9 | 8.7 | 6.7 | 6.3 | 80.2 | 80.8 | 4.1 | 4.2 |
| $K_2Ni(IO_3)_4 \cdot 2H_2O$ | 8.9 | 8.4 | 6.7 | 6.4 | 80.2 | 80.1 | 4.1 | 4.5 |
| $K_2Zn(IO_3)_4 \cdot 2H_2O$ | 8.8 | 8.9 | 7.4 | 7.5 | 79.6 | 79.1 | 4.1 | 4.0 |

EXPERIMENTAL DATA AND DISCUSSION

The DTA and TG curves of the three double salts are shown in Fig. 1, while their DSC curves are shown in Fig. 2. Table 2 contains data about the
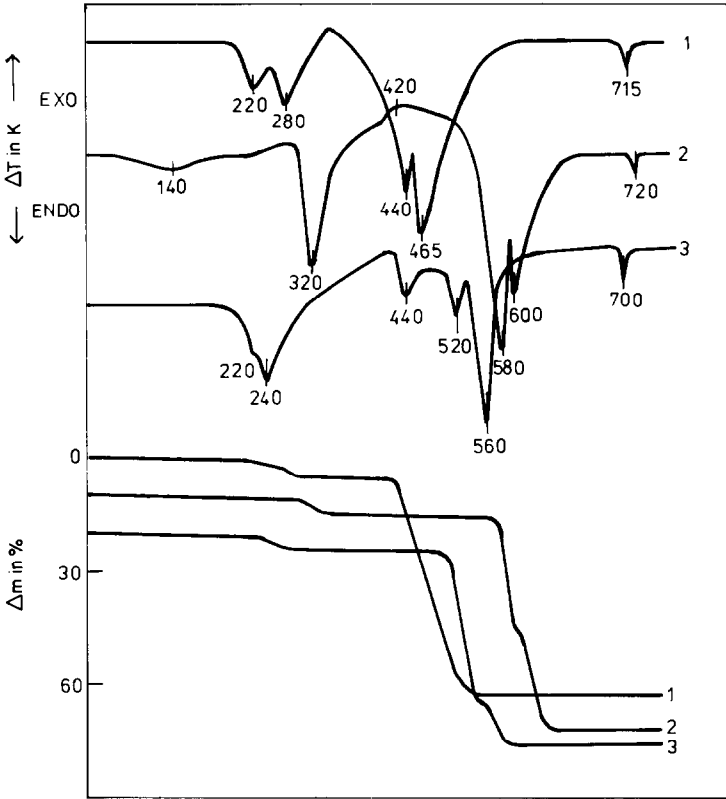
Fig. 1. DTA and TG curves of 1, $K_2Co(IO_3)_4 \cdot 2H_2O$; 2, $K_2Ni(IO_3)_4 \cdot 2H_2O$; 3, $K_2Zn(IO_3)_4 \cdot 2H_2O$.
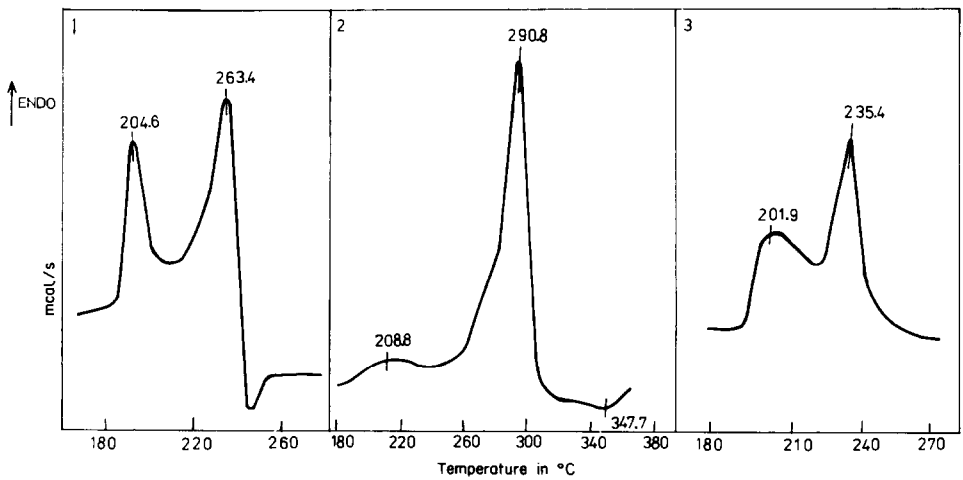


Fig. 2. DSC curves of 1, $K_2Co(IO_3)_4 \cdot 2H_2O$; 2, $K_2Ni(IO_3)_4 \cdot 2H_2O$; 3, $K_2Zn(IO_3)_4 \cdot 2H_2O$.

TABLE 2

Data for the dehydration and decomposition to simple iodates of $K_2Me(IO_3)_4 \cdot 2H_2O$ (where $M^{2+}$ is $Co^{2+}$, $Ni^{2+}$, $Zn^{2+}$) from DTA, TG and DSC curves

| Compound | Phase transition | Data from DTA | | | Data from DSC | | |
|---|---|---|---|---|---|---|---|
| | | $T_{max}/$ °C | $\Delta m/\%$ | | $T/$°C | | $\Delta H_{ph.tr.}^{\ominus}/$ kJ mol$^{-1}$ |
| | | | Calc. | Exp. | Onset | Max. | |
| $K_2Co(IO_3)_4 \cdot 2H_2O$ | $K_2Co(IO_3)_4 \cdot 2H_2O \rightarrow KIO_3 + Co(IO_3)_2 + 2H_2O$ | 220 <br> 280 | 4.1 | 4.2 | 245.7 | 204.6 } <br> 263.4 } | 143.6 |
| $K_2Ni(IO_3)_4 \cdot 2H_2O$ | $K_2Ni(IO_3)_4 \cdot 2H_2O \rightarrow$ unidentified phase transition | 140 | 4.1 | 4.2 | 194.8 | 208.8 | 11.1 |
| | $K_2Ni(IO_3)_4 \cdot 2H_2O \rightarrow KIO_3 + Ni(IO_3)_2 + 2H_2O$ | 320 | | | 275.8 | 290.8 | 180.3 |
| | $\alpha\text{-}Ni(IO_3)_2 \rightarrow \beta\text{-}Ni(IO_3)_2$ | 420 | | | 331.4 | 347.4 | −8.4 |
| $K_2Zn(IO_3)_4 \cdot 2H_2O$ | $K_2Zn(IO_3)_4 \cdot 2H_2O \rightarrow KIO_3 + Zn(IO_3)_2 + 2H_2O$ | 220$^a$ <br> 240 | 4.1 | 4.3 | 194.3 <br> — | 201.9 } <br> 235.4 } | 150.6 |

$^a$ Shoulder

temperatures and the enthalpies of the phase transitions recorded from the corresponding curves, while Table 3 contains the kinetic data.

The DTA and TG curves of the three investigated compounds (Fig. 1) show first of all a strong endo effect, with a clearly formed shoulder in $K_2Zn(IO_3)_4 \cdot 2H_2O$, which it appears split in $K_2Co(IO_3)_4 \cdot 2H_2O$ while in $K_2Ni(IO_3)_4 \cdot 2H_2O$ it is preceded by a diffuse and small endo effect. It follows from the corresponding TG curves, according to the change in the mass ($\Delta m$), and that this peak corresponds to the complete dehydration of the compounds. However, in the TG curves of $K_2Co(IO_3)_4 \cdot 2H_2O$ there is a bend which, according to the calculations, may be assumed to be connected with stepwise dehydration to monohyrate, although this has not been isolated.

Samples were isolated and identified by X-ray analysis, the aim being to expand the information in relation to the phase transition examined, after its final completion. The diffractograms obtained reveal accurately the reflections of the respective simple anhydrous salts ($KIO_3$ and $M(IO_3)_2$) which are different from those of the initial $K_2M(IO_3)_4 \cdot 2H_2O$. The pattern is analogous in all three investigated compounds.

For the purpose of illustration, Figure 3 compares the X-ray data for $K_2Co(IO_3)_4 \cdot 2H_2O$ and for a sample isolated at $T = 400°C$ (after the TG curve) with those for $KIO_3$ and $Co(IO_3)_2$. The interplanar distances $d$ for the last two salts are taken from published sources [9, 10]. From these data it is possible to draw the conclusion that the first observed effect in the derivatograms is due both to a process of complete dehydration and to a process of decomposition of the double salt to $KIO_3$ and $Co(IO_3)_2$. The two processes take place simultaneously or immediately after each other, but the resolution of the DTA method does not allow their separate recording. This specificity of the phase transition examined can also explain the

TABLE 3

Kinetic data for the dehydration and decomposition to simple iodates of $K_2M(IO_3)_4 \cdot 2H_2O$ (where $M^{2+}$ is $Co^{2+}$, $Ni^{2+}$, $Zn^{2+}$)

| Compound | $T_{max}^a/$ °C | $E^*/$ kJ mol$^{-1}$ | ln ($A/$ s$^{-1}$) | Kinetic equation $F(\alpha)$ | Corre-lation coeff. | Stand-ard devi-ation | $\Delta H_{ph.tr.}^{\ominus \, b}/$ kJ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|
| $K_2Co(IO_3)_4 \cdot 2H_2O$ | | | | | | | |
| Step I | 220 | 103.2 | 18.9 | $(1-\alpha)^{1/3}$ | 0.998 | 0.018 ⎱ | 143.6 |
| Step II | 280 | 153.8 | 28.4 | $(1-\alpha)$ | 0.938 | 0.315 ⎰ | |
| $K_2Ni(IO_3)_4 \cdot 2H_2O$ | 320 | 203.7 | 37.9 | $(1-\alpha)$ | 0.979 | 0.175 | 180.3 |
| $K_2Zn(IO_3)_4 \cdot 2H_2O$ | 240 | 115.9 | 21.6 | $(1-\alpha)^{1/2}$ | 0.998 | 0.049 | 150.6 |

$^a$ DTA. $^b$ DSC.
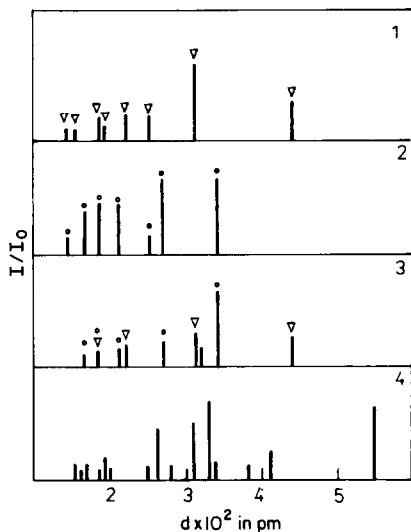
Fig. 3. X-Ray powder data of 1, $KIO_3$; 2, $Co(IO_3)_2$; 3, sample isolated at $T = 400°C$ (from DTA); 4, $K_2Co(IO_3)_4 \cdot 2H_2O$.

character of the peak of the first endoeffect at $K_2Zn(IO_3)_4 \cdot 2H_2O$ and $K_2Co(IO_3)_4 \cdot 2H_2O$.

Two peaks with common foundation (Fig. 2, curve 3) are recorded in the DSC curve of $K_2Zn(IO_3)_4 \cdot 2H_2O$ due to the higher resolution of this method, instead of the shoulder observed in the derivatogram in the first peak ($T = 220°C$). The DSC curve of $K_2Co(IO_3)_4 \cdot 2H_2O$ (Fig. 2, curve 1) is also analogous. This character of the peaks does not provide for accurate recording of the change in the enthalpy ($\Delta H^{\ominus}_{ph.tr.}$) for each of them separately. Its values could provide certain information about their nature. The lack of such information makes it difficult to give an unequivocal reply (along the DTA curves as well) about how and in what sequence the processes of dehydration and decomposition of these compounds occur.

The DSC curve of $K_2Ni(IO_3)_4 \cdot 2H_2O$ appears to be more complicated (Fig. 2, curve 2). First of all it shows a relatively weak, though well differentiated, endo effect with $T_{max} = 208.8°C$ and $\Delta H^{\ominus}_{ph.tr.} = 11.1$ kJ mol$^{-1}$. This could be due to decomposition of the double salt to simple iodates, but such an assumption is not acceptable, because the DSC curves of the investigated $Ni(IO_3)_2 \cdot 2H_2O$, or its deuterated analogue $Ni(IO_3)_2 \cdot 2D_2O$ [11] show an analogous effect with $4H^{\ominus}_{ph.tr.} = 6.4$ kJ mol$^{-1}$, but it has not been unambiguously identified. The same endo effect in the DSC curve with $T_{max} = 290.8°C$ ($T_{onset} = 275.8°C$ corresponds to the dehydration and decomposition of $K_2Ni(IO_3)_4 \cdot 2H_2O$, the recorded value $\Delta H^{\ominus}_{ph.tr.}$ being higher than for the two other compounds. This is to be explained by the higher value of CFSE for $Ni^{2+}$, compared with that for $Co^{2+}$, while in $Zn^{2+}$
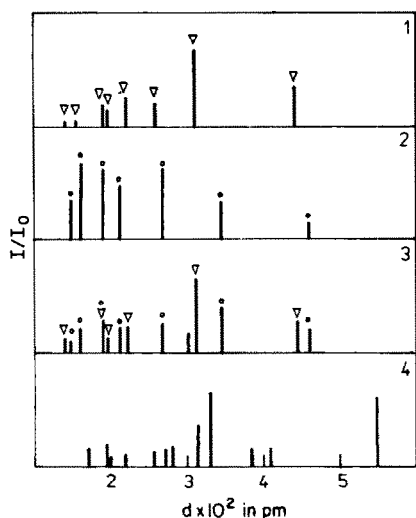
Fig. 4. X-ray powder data of 1, $KIO_3$, 2, $\beta$-$Ni(IO_3)_2$; 3, sample isolated at $T = 450°C$ (from DTA); 4, $K_2Ni(IO_3)_4 \cdot 2H_2O$.

the CFSE is 0 [5]. This value of CFSE at $Ni^{2+}$ leads to stabilization of its polyhedron in the crystal structure of the compound.

It follows from what has been stated above that the change in the enthalpy of dehydration ($\Delta H_{ph.tr.}^{\ominus}$) recorded along the DSC curves (Table 2) includes both $\Delta H_{dehyd}^{\ominus}$ and $\Delta H_{decomp}^{\ominus}$ of the investigated compounds.

After the effects of dehydration and decomposition there appears a slight exo effect in the DSC curve of $K_2Ni(IO_3)_4 \cdot 2H_2O$ at $T = 347.4°C$ with a corresponding value of $\Delta H^{\ominus} = -8.7 \text{ kJ mol}^{-1}$. This is also observed in the DTA curve ($T_{max} = 420°C$) and may be ascribed to the polymorphous transition $\alpha$-$Ni(IO_3)_2 \rightarrow \beta$-$Ni(IO_3)_2$, as described in pertinent literature [11, 12]. It is proved also from the diffractogram of a sample isolated by us using DTA at $T = 450°C$ which shows a mixture of $KIO_3$ and $\beta$-$Ni(IO_3)_2$ (Fig. 4). The data about $\beta$-$Ni(IO_3)_2$ are from ref. 10.

The DTA curve of $K_2Zn(IO_3)_4 \cdot 2H_2O$ (Fig. 1, curve 3) shows an endo effect with $T_{max} = 440°C$ which is due to melting of the mixture of $KIO_3$ and $Zn(IO_3)_2$ obtained after dehydration. An analogous endo effect is absent in the corresponding curve of $K_2Co(IO_3)_4 \cdot 2H_2O$ and of $K_2Ni(IO_3)_4 \cdot 2H_2O$, but instead there is a slight expansion in the upper part of the peak corresponding to the next endo effect. This expansion is particularly apparent in the curve of $K_2Co(IO_3)_4 \cdot 2H_2O$ (Fig. 1, curve 1) and may be explained by fusion of the two endo effects. One proof in favour of this assumption is the visually observable melting of the mixtures obtained after the decomposition, in the three investigated compounds.

In the further course of the DTA curves it is very easy to distinguish the effect of decomposition of the $M(IO_3)_2$ from that of $KIO_3$. Decomposition takes place along routes described in pertinent literature, namely $M(IO_3)_2 \rightarrow MeO + I_2 + 5/2O_2$ where $M^{2+}$ is $Co^{2+}$, $Ni^{2+}$, $Zn^{2+}$ [13]. Two

decomposition pathways are possible in $KIO_3$ [14, 15], $KIO_3 \rightarrow KI + (3/2)O_2$ and $2KIO_3 \rightarrow K_2O + I_2 + (5/2)O_2$, the reaction along the second pathway taking place to a much smaller extent.

Taking into account the manner of deposition of $KIO_3$ it becomes clear that it is not possible to compare $\Delta m_{exp}$ with $\Delta m_{calc}$. For instance, for the $K_2Zn(IO_3)_4 \cdot 2H_2O$ along the TG curve we record $\Delta m = 56.0\%$, compared to the $\Delta m = 57.3\%$ calculated with the first equation. Analysis of the experimental data in this direction indicates that in the three compounds investigated by us the decomposition of $KIO_3$ takes place to a different degree along the second pathway.

The last peak which appears in the DTA curves of $K_2Zn(IO_3)_4 \cdot 2H_2O$ at 700°C, of $K_2Co(IO_3)_4 \cdot 2H_2O$ to 715°C and of $K_2Ni(IO_3)_4 \cdot 2H_2O$ at 720°C may be ascribed, according to ref. 16, to the effect of melting of KI obtained in the process of decomposition.

On the basis of the data from the TG curves, by means of a computer programme, calculations were made of the formal kinetic parameters ($E^*$ and $A$) in relation to the first endo effect characterizing the processes of dehydration and decomposition of the initial double salts to simple iodates. On the basis of 25 kinetic equations known from published sources and introduced into the programme [17, 18] it was possible to determine the one which characterizes the phase transition. A differential method was used for kinetic analysis of nonisothermal data [17]. The values obtained for $E^*$ and $A$ are presented in Table 3.

The data from Table 3 show that the calculated values of $E^*$ correlate with the $T_{max}$, recorded from the DTA curves, of the respective endo effects corresponding to the dehydration and decomposition of the double salt to simple iodates. The corresponding kinetic equations are of the $(1 - \alpha)^n$ type and they show that the investigated processes take place in the kinetic region.

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