

**THERMAL STABILITIES OF NEW  
COMPLEXES OF MAGNESIUM NITRATE,  
ACETATE AND PHOSPHATE  
WITH AMIDE LIGANDS**

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The thermal decompositions of complex compounds of magnesium nitrate, acetate and phosphate with urea, acetamide and formamide ligands were investigated by means of simultaneous TG-DTA. The thermal stabilities of the complexes depend on the natures of the anions and the amide ligands.

The thermal stabilities of coordination compounds  $MgL_n(H_2O)_mX_2$ , where  $L = CO(NH_2)_2$ ,  $CH_3CONH_2$  or  $HCONH_2$ ,  $X = NO_3^-$ ,  $CH_3COO^-$  or  $H_2PO_4^-$ ,  $m = 0, 1, 2, 4$  or  $6$  and  $n = 1, 2, 4$ , or  $6$ , were studied by means of TG, IR spectroscopic, chemical and X-ray diffraction methods.

On the basis of the results of thermogravimetric investigations and studies of the decomposition intermediates, mechanisms of thermal decomposition of the complexes were proposed.

**Experimental results and discussion**

The thermogravimetric and differential thermal analysis of the complexes was carried out on a derivatograph. The standard heating rate ( $10 \text{ deg min}^{-1}$ ) was monitored with a programmed LP-980 regulator.

The individual character of the intermediates of thermal decomposition was corroborated via chemical, X-ray diffraction and IR spectroscopic analyses.

DTA and TG results are listed in the Table.

The heating curve of  $2CO(NH_2)_2 \cdot Mg(CH_3COO)_2$  exhibits endoeffects at  $155^\circ$  and  $240^\circ$ , and an exoeffect at  $475^\circ$ . The endoeffect at  $155^\circ$  is consistent with melting of the complex, which was confirmed by visual observations at the given

**Table 1** The experimental results on thermal stability of complex compounds

Compound	Melting		Dehydration, decomposition		Transitions		Total mass loss, %	Final product of thermolysis
	<i>t</i> , °C	<i>m</i> , %	<i>t</i> , °C	<i>m</i> , %	<i>t</i> , °C	<i>m</i> , %		
2CO(NH <sub>2</sub> ) <sub>2</sub> · Mg(CH <sub>3</sub> COO) <sub>2</sub>	155	—	240	43.33	475	41.50	84.83	MgO
2CO(NH <sub>2</sub> ) <sub>2</sub> · Mg(NO <sub>3</sub> ) <sub>2</sub> · 4H <sub>2</sub> O	95	—	180, 260	72.50	380	15.75	88.25	MgO
4CO(NH <sub>2</sub> ) <sub>2</sub> · Mg(NO <sub>3</sub> ) <sub>2</sub> · 2H <sub>2</sub> O	110	—	180, 280	54.17	420	36.11	90.28	MgO
4CO(NH <sub>2</sub> ) <sub>2</sub> · Mg(NO <sub>3</sub> ) <sub>2</sub>	125	—	275	55.38	430	33.85	89.28	MgO
6CO(NH <sub>2</sub> ) <sub>2</sub> · Mg(NO <sub>3</sub> ) <sub>2</sub>	135	—	280	70.90	420	21.28	92.18	MgO
4CO(NH <sub>2</sub> ) <sub>2</sub> · Mg(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	150	15.18	200, 240	29.46	345	11.61	56.25	[Mg(PO <sub>3</sub> ) <sub>2</sub> ] <sub>n</sub>
4CH <sub>3</sub> CONH <sub>2</sub> · Mg(NO <sub>3</sub> ) <sub>2</sub> · 2H <sub>2</sub> O	45	—	195	34.31	390	55.89	90.20	MgO
6CH <sub>3</sub> CONH <sub>2</sub> · Mg(NO <sub>3</sub> ) <sub>2</sub> · 2H <sub>2</sub> O	110	—	230	60.98	410	31.33	92.31	MgO
4HCONH <sub>2</sub> · Mg(CH <sub>3</sub> COO) <sub>2</sub>	130	—	260	55.56	450, 570	32.22	87.78	MgO
HCONH <sub>2</sub> · Mg(CH <sub>3</sub> COO) <sub>2</sub>	145	—	260	24.17	450, 570	54.99	79.16	MgO

temperature, and by the deviation of the electric conductivity line from zero, and is in good agreement with the studied melting diagram of the CO(NH<sub>2</sub>)<sub>2</sub>–Mg(CH<sub>3</sub>COO)<sub>2</sub> system.

Chemical analysis of the intermediate samples produced by isothermal treatment at the corresponding temperatures indicated that the endoeffect at 240° corresponds to decomposition and removal of urea, with formation of the oxo salt Mg<sub>4</sub>O(CH<sub>3</sub>COO)<sub>6</sub>.

Heating above 400° results in decomposition of this oxo salt. The newly formed MgO undergoes a phase transition, which is manifested in the form of an exoeffect at 475° (mass loss 84.83%).

The TG–DTA diagrams obtained for the urea complexes of magnesium nitrate, 2CO(NH<sub>2</sub>)<sub>2</sub> · Mg(NO<sub>3</sub>)<sub>2</sub> · 4H<sub>2</sub>O, 4CO(NH<sub>2</sub>)<sub>2</sub> · Mg(NO<sub>3</sub>)<sub>2</sub> · 2H<sub>2</sub>O, 4CO(NH<sub>2</sub>)<sub>2</sub> · Mg(NO<sub>3</sub>)<sub>2</sub> and 6CO(NH<sub>2</sub>)<sub>2</sub> · Mg(NO<sub>3</sub>)<sub>2</sub>, were analogous, the endoeffects at 95°, 110°, 125° and 135° being consistent with melting of the corresponding compounds without mass loss. The endothermic effects at 180° in the heating curves of the hydrated urea complexes correspond to the removal of crystallization water with partial decomposition of urea. The endothermic effects at 260–280° are typical of decomposition with the removal of urea. The pronounced exothermic effects at 380–430° correspond to thermooxidation reactions of

magnesium nitrate, and interaction between the organic urea decomposition products and nitrogen dioxide, with the formation of nitrosyl compounds. The given redox process is explosive in character, the number of exothermic peaks and their values increasing with the accelerating heating rate in the event of direct contact of the sample and a platinum thermocouple, due to the catalytic effect of the latter. Magnesium oxide is the final product of the thermal decompositions of the above urea nitrate compounds (mass loss 88.25%, 90.28%, 89.28% and 92.18%, respectively).

The TG-DTA diagram of  $4\text{CO}(\text{NH}_2)_2 \cdot \text{Mg}(\text{H}_2\text{PO}_4)_2$  displays four exothermic effects, at 150°, 200°, 240° and 345°. The effect at 150° corresponds to the incongruent melting of the compound, with partial decomposition of magnesium phosphate to acid magnesium pyrophosphate. The process is accompanied by the evolution of ammonia, due to the decomposition of urea (mass loss 15.18%). At 200–240°, urea is released and decomposed, and monomagnesium phosphate is completely transformed into acid pyrophosphate (mass loss 29.46%). The endoeffect at 345° corresponds to two processes: complete removal of the decomposition products of urea ( $\text{NH}_3$  and  $\text{CO}_2$ ), and formation of a mixture of condensed phosphates with different degrees of phosphate anion polymerization (mass loss 11.61%). The final decomposition product is a cyclic magnesium tetrametaphosphate of  $[\text{Mg}(\text{PO}_3)_2]_n$  type (total mass loss 56.25%).

The decomposition temperatures of urea and monomagnesium phosphate tetrahydrate are lower than that of  $4\text{CO}(\text{NH}_2)_2 \cdot \text{Mg}(\text{H}_2\text{PO}_4)_2$ . This indicates the higher thermal stability of the complex.

It should be noted that the TG-DTA diagrams of the urea complexes did not exhibit the endothermic effect at 400° that is typical of urea and corresponds to the decomposition of cyanuric acid to  $\text{CO}_2$  and melamine:  $2(\text{CONH})_3 \rightarrow (\text{H}_2\text{NCN})_3 + 3\text{CO}_2$ . Thus, the mechanism of thermal decomposition of coordinated urea should be different.

The TG-DTA diagrams of the acetamide complexes  $4\text{CH}_3\text{COMH}_2 \cdot \text{Mg}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  and  $6\text{CH}_3\text{CONH}_2 \cdot \text{Mg}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  revealed endothermic effects at 45° and 110°, due to congruent melting of the complexes. The endoeffects at 195° and 230° (for  $4\text{CH}_3\text{CONH}_2 \cdot \text{Mg}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  and  $6\text{CH}_3\text{CONH}_2 \cdot \text{Mg}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ , respectively) indicate the loss of two water molecules and decomposition of the compounds, with simultaneous removal of the decomposition products. The intense exoeffects at 390 and 410° correspond to the formation of nitrosyl compounds. On further heating,  $\text{MgO}$  is formed (mass loss 90.20% and 92.31%, respectively).

The thermal decomposition processes for the formamide complexes of magnesium acetate are identical. The complexes  $4\text{HCONH}_2 \cdot \text{Mg}(\text{CH}_3\text{COO})_2$  and  $\text{HCONH}_2 \cdot \text{Mg}(\text{CH}_3\text{COO})_2$  melt at 130° and 145°, respectively. Splitting-off and

stepwise removal of formamide with intermediate of formation the oxo salt  $Mg_4O(CH_3COO)_6$  occurs at  $260^\circ$  (mass loss 55.56% and 24.17%, respectively). On further heating, the oxo salt is decomposed to the final product (MgO); in the TG-DTA diagrams, this corresponds to exoeffects at  $570^\circ$  (total mass loss 87.78% and 79.16%, respectively).

## Conclusion

It can be concluded from the thermoanalysis data on the amide complexes of these magnesium salts that their thermal decompositions are accompanied by breakdown of the anion and organic components. The thermal stabilities of these compounds and the character of their decomposition depend on the natures of the amide ligand and the acidic residue.

It was also established that the thermal stabilities of the urea and acetamide complexes decrease with decreasing number of organic ligand molecules in the inner sphere of the central metal atom. The reverse dependence was observed for the formamide compounds, i.e. the melting temperatures of these complexes decrease with increasing number of coordinated formamide molecules.

## References

- 1 V. T. Orlova, I. N. Lepeshkov, V. I. Kosterina and E. A. Konstantinova, *J. Neorgan. Khim.*, 27 (1982) 1050.
- 2 V. I. Kosterina, V. T. Orlova and I. N. Lepeshkov, *J. Neorgan. Khim.*, 28 (1983) 1841.
- 3 V. T. Orlova, J. B. Kudinov, V. I. Kosterina, N. K. Semendyaeva and I. N. Lepeshkov, *J. Thermal Anal.*, 30 (1985) 1047.
- 4 V. T. Orlova, V. I. Kosterina and I. N. Lepeshkov, *J. Neorgan. Khim.*, 30 (1985) 1877.
- 5 O. E. Artemova, V. T. Orlova and I. N. Lepeshkov, *J. Neorgan. Khim.*, 30 (1985) 1072.

**Zusammenfassung** — Die thermische Zersetzung der Komplexverbindungen von Magnesiumnitrat-, acetat und -phosphat mit Harnstoff, Acetamid und Formamid wurden durch simultane TG-DTA untersucht. Die thermische Stabilität der Komplexe hängt von den Anionen des Salzes und den Amidliganden ab.

**Резюме** — Совмещенным методом ТГ и ДТА изучено термическое разложение комплексов нитрата-, ацетата- и фосфата магния с мочевиной, ацетамидом и формамидом. Термоустойчивость комплексов зависит как от природы аниона, так и лиганда.