

THERMAL STABILITY OF UREA COMPLEXES OF MAGNESIUM NITRATE AND MAGNESIUM MONOPHOSPHATE

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Urea complexes of magnesium nitrate and magnesium monophosphate were synthesized and investigated by thermal analysis, X-ray phase analysis and IR spectroscopy. It was found that the thermal stability of the complexes increases with the number of organic ligands in the complex. The mass losses corresponding to the stages of thermal decomposition of the compounds were calculated via the thermogravimetric curves. The mode of coordination between urea and Mg^{II} was investigated by IR spectroscopy.

Studies on the interactions between magnesium nitrate or magnesium monophosphate and urea in aqueous solution form part of the investigations of more complex processes with the aim of solving problems associated with the manufacture of complex fertilizers from dolomite and magnesium-containing wastes of phosphate production [1, 2].

The urea complexes $2CO(NH_2)_2 \cdot Mg(NO_3)_2 \cdot 6H_2O$ (I), $2CO(NH_2)_2 \cdot Mg(NO_3)_2 \cdot 4H_2O$ (II), $4CO(NH_2)_2 \cdot Mg(NO_3)_2 \cdot 2H_2O$ (III), $6CO(NH_2)_2 \cdot Mg(NO_3)_2$ (IV) and $4CO(NH_2)_2 \cdot Mg(H_2PO_4)_2$ (V) have been synthesized on the basis of equilibrium studies of aqueous systems of magnesium nitrate, magnesium monophosphate and urea [3, 4]. The compounds have better physico-mechanical properties than those of mechanical blends of the initial components, and they contain several nutrient elements for plants: N, P and Mg.

The thermal behaviour of the compounds was studied in order to elucidate the effects of composition and structure on the stability. The experimental results may be utilized in practice in the production of the above compounds.

Experimental and discussion of results

A Paulik–Paulik–Erdey derivatograph system was used for thermal analysis; the heating rate was 10 deg/min. Chemical, X-ray phase, crystal–optical and IR spectroscopic methods of analysis were applied to identify the urea complexes and the products of their thermal decomposition.

The thermoanalytical curves of compounds I, II, III and IV are presented in Figs 1–4. The congruent melting temperatures increase from 90 to 135° with the number

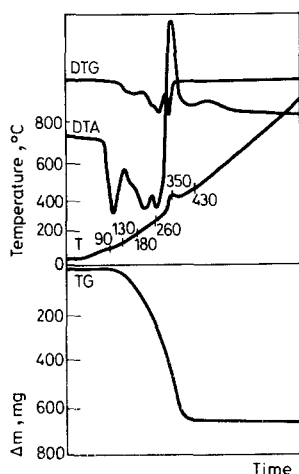


Fig. 1 Thermal curves of $2\text{CO}(\text{NH}_2)_2 \cdot \text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (I)

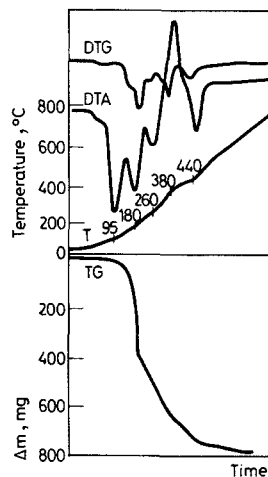


Fig. 2 The thermal curves of $2\text{CO}(\text{NH}_2)_2 \cdot \text{Mg}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (II)

of organic ligands in the molecule. This finding is indicative of more stable bonds between magnesium and urea molecules than between magnesium and water molecules. As may be seen in Figs 2 and 3, combined water from complexes II and III is released at a rather high temperature, 180°, and it may therefore be assumed that the water molecules in these compounds are located in the inner sphere, in contrast to complex I (Fig. 1), from which water release starts at 130°. This confirms that in compounds II, III and IV urea and water molecules are located in the inner sphere, while in compounds I two urea molecules and four water molecules are located in the inner sphere and two water molecules in the outer coordination sphere. The release of water from the complexes is accompanied by a partial decomposition of the urea, ammonia being evolved. For complexes I, II and III, the mass losses are 32.44, 50.00 and 17.36 mass %, respectively.

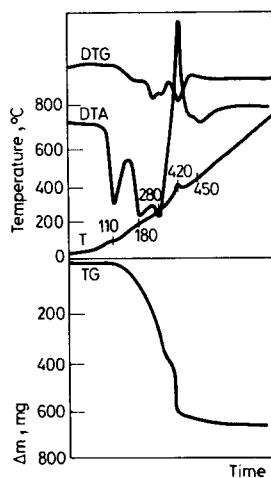


Fig. 3 Thermal curves of $4\text{CO}(\text{NH}_2)_2 \cdot \text{Mg}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (III)

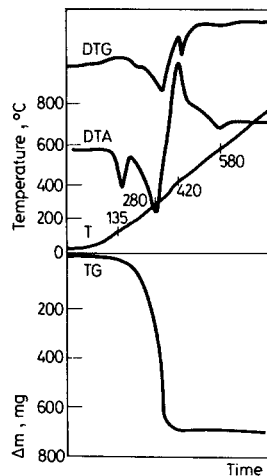


Fig. 4 Thermal curves of $6\text{CO}(\text{NH}_2)_2 \cdot \text{Mg}(\text{NO}_3)_2$ (IV)

The following endothermic effect at 260–280° in the heating curves of the complexes (cf. Figs 1–4) characterizes their decomposition, with partial evolution of the decomposition products of urea, and the formation of cyanuric acid and melamine. For complexes I, II, III and IV, the mass losses are 21.62, 22.50, 36.81 and 70.90 mass %, respectively.

In the temperature interval between 350 and 420°, a sharp pronounced exothermic effect is observed; it is associated with an explosion-like oxidation-reduction process. In this process, the organic decomposition products of urea react with nitrogen evolved in the decomposition of magnesium nitrate and form intermediate nitrosyl compounds. For complexes I, II, III and IV, the mass losses corresponding to the exothermic process are 35.39, 16.50, 33.33 and 21.28 mass %, respectively, while the total mass losses are 89.55, 88.25, 90.28 and 92.18 mass % the corresponding theoretical values are 89.28, 88.15, 90.50 and 92.07 mass %, respectively. The final solid thermal decomposition product of the urea complexes is magnesia.

The thermal analysis curves of complex V are shown in Fig. 5. The curves indicate four endothermic effects, at 150, 200, 240 and 345°. The peak at 150° corresponds to incongruent melting of the compound, associated with partial decomposition of magnesium monophosphate. The process is also accompanied by ammonia evolution, due to urea decomposition. The mass loss is 15.18 mass %. At 200 and 240°, cyanuric acid is formed and polymerization of the urea decomposition products proceeds. Simultaneously, magnesium orthophosphate is transformed

into the acid pyrophosphate. The mass loss is 29.46 mass %. The endothermic effect at 345° corresponds to the superposition of two processes: the total elimination of the urea decomposition products NH_3 and CO_2 , and the formation of a mixture of condensed phosphates involving different polymerization degrees of the phosphate anions [5]. The mass loss is 11.61 mass %. The final solid product of

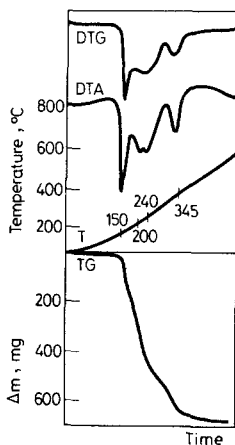


Fig. 5 Thermal curves of $4\text{CO}(\text{NH}_2)_2 \cdot \text{Mg}(\text{H}_2\text{PO}_4)_2$ (V)

decomposition is a cyclic magnesium tetrametaphosphate of the type $[\text{Mg}(\text{PO}_3)_2]_n$. The overall mass loss when complex V is heated to 600° is 60.61 mass % (theoretical value 60.22 mass %).

X-ray phase analyses of all compounds and their decomposition products were performed with a DRON-1,0 instrument using CuK_α radiation and a nickel filter. The diffraction diagrams obtained confirmed the assumed mechanism of thermal decomposition of the complexes.

IR spectroscopy was used to identify the compounds obtained and also to determine the mode of metal-ligand coordination. IR spectra were recorded with a Zeiss UR-20 spectrophotometer in the frequency range 3400 to 4000 cm^{-1} . The samples were tablets pressed with KBr. From the shifts in the CO and CN valence vibration bands, it may be concluded that the metal-urea bond in the complexes studied involves the oxygen atom of the carbonyl group.

References

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Zusammenfassung — Harnstoffkomplexe von Magnesiumnitrat und Magnesiummohosphat wurden synthetisiert und mittels thermischer Analyse, Röntgenphasenanalyse und IR-Spektroskopie untersucht. Die thermische Stabilität der Komplexe nimmt mit der Zahl der organischen Liganden im Komplex zu. Die thermischen Zersetzungsschritten der Verbindungen entsprechenden Massenverluste wurden aus den thermogravimetrischen Kurven ermittelt. IR-spektroskopisch wurde die Art der Koordination zwischen Harnstoff und Mg(II) untersucht.

Резюме — Синтезированы и исследованы методами ДТА, РФА, ИКС карбамидные комплексы нитрата и монофосфата магния. Установлено, что с увеличением числа молекул органического лиганда в комплексах термоустойчивость последних повышается. По термогравиметрической кривой рассчитаны изменения массы, соответствующие стадиям термолиты полученных соединений. На основании данных ИК спектроскопии рассмотрен способ координации карбамида по отношению к Mg^{II} .