Thermochimica Acta, 92 (1985) 485-487
Elsevier Science Publishers B.V., Amsterdam

TOPOCHEMISTRY OF THERMAL DEHYDRATION OF SYNGENITE $K_2Ca(SO_4)_2.H_2O$

Krystyna Wieczorek-Ciurowa
Technical University of Cracow, 31-155 Cracow, Poland

ABSTRACT

On the basis of thermogravimetry, optical observations, scanning electron microscopy, IR spectroscopy, X-ray diffraction as well as physico-chemical properties of reactant and product, it was established that the process of the dehydration of syngenite has a topochemical character.

INTRODUCTION

The thermal decomposition of crystal hydrates is a typical heterogeneous reaction of the type solid A   solid B + gas. The dehydration of syngenite, $K_2Ca(SO_4)_2.H_2O$, is a good example of such a reaction. Syngenite is an intermediate during the processing naturally-occuring polihalite, $K_2Ca_2Mg(SO_4)_4.$ $.2H_2O$, into fertilizers /1/.

It would not be unreasonable to assume that thermal decomposition of solid crystalline compounds associated with structural rearrangements without the destruction of the basic crystal lattice has no influence on chemical reactivity of the product. If such an assumption could be made it would be interesting from the technological point of view.

If correct conclusions on the kinetics and mechanisms of such reactions, the factors determining the pathway of the topochemical process of decomposition must be known /2,3/. Therefore an attemp was made to find the relationship between the structure of crystal hydrate and the morfology of anhydrous compound. It is known that course of such reactions depends not only on geometric factors but also on the nature of bonds between the atoms and especially on the energy of thermal dissociation.

The process of dehydration of $K_2Ca(SO_4)_2.H_2O$ was investigated using thermogravimetric and as well as optical methods and electron microscopy, IR spectroscopy and X-ray diffraction.

EXPERIMENTAL

Equipment and methods of measurement

Thermal analysis was carried out using a Q-Derivatograph (Hungarian Optical Works) employing a dynamic heating programme (heating rate 5 deg.min^{-1}) /4/, the sample size being 300 mg. Phases identification was based on powder X-ray diffraction patterns (TUR-M-61), Ca-K   radiation, on IR spectra recorded with a Zeiss UR-20 spectrophotometer using pellets in KBr and on scanning electron microscope results (JEOL).

Proceedings of ICTA 85, Bratislava

Material

Synthetic syngenite $K_2Ca(SO_4)_2.H_2O$ was crystallized at 298 K from aqueous solutions of potassium and calcium sulphates. On evaporation a finely-divided crystalline colourless product is obtained. The crystalls have the form of elongated prisms with typical two dimension 0.14 mm and 0.01 mm /2,3/.

RESULTS AND DISCUSSION

A. Thermal analysis: Simultaneous TG-DTG-DTA curves shown in Fig. 1 (only for illustration) are typical and cover the entire process of dehydration of syngenite in air. It can be seen that the dehydration of $K_2Ca(SO_4)_2.H_2O$ is a one step endothermic process occuring in the temperature range 423 – 573 K leading formation of the anhydrous compound stable up to 673 K. It can be makes isolated and characterized further by different techniques.

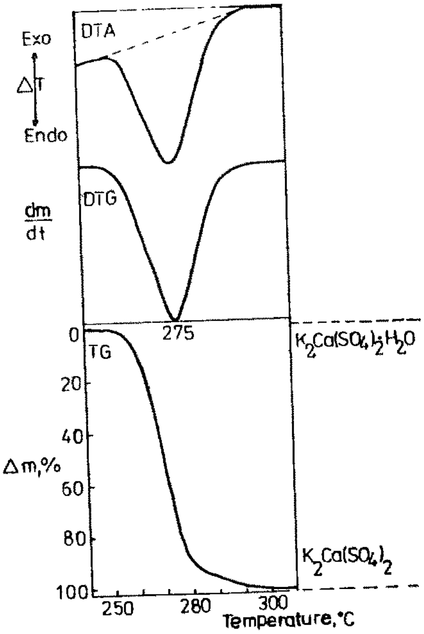

Fig. 1: Simultaneous TG, DTG and DTA curves of the syngenite dehydration traced using open crucible

B. Infrared study: The results of IR studies of syngenite before and after dehydration are discussed below. The spectrum of the original compound exhibits significant bands at 3320 and 3380 cm^{-1} attributed to the O-H fully-symmetric stretching (of type A_1 – $_1$) and antisymmetric stretching (of type B_1 – $_2$). The 1685 cm^{-1} band corresponds to fully-symmetric binding of H-O-H of type A_1 – $_2$. These bands were not observed in the spectrum of the anhydrous sample (as it expected). The dehydration does not cause appreciable changes in the 1100 cm^{-1} band characteristic of the SO_4^{2-} ion valence vibration, the band on the 600 cm^{-1} region is, however, narrower and distorted. Moreover, the characteristic bands observed for the original compound at 442 cm^{-1} (weak) attributed to the H-O-H liberation motion ("hindered" rotation (and at 760 cm^{-1}) strong, sharp) indicating the presence of hydrogen bonds in syngenite are conspiciously absent in the spectrum obtained after dehydration. It is thus apparent that the water in syngenite is lattice water. The removal of such water should occur without complete destruction of the original lattice, because the water molecules influence the second coordination sphere. It is concluded that the changes in the IR spectrum of syngenite brought about by the dehydration indicate changes in the symmetry of the oscilating groups of atoms associated with forced degenerated vibrations.

C. Geometrical considerations: Microscopic inspections indicate that the habit of the crystals is preserved during dehydration. This rises the question how the water molecules diffuse out of the lattice without disturbing the co-ordination polyhydra. Syngenite has a layer structure with a net-work of channels. The water molecules adjacent to K, Ca and O are within spaces of dimensions greater than 5.5 Å which allows them to move freelly - diffuse within lattice. This is confirmed by the fact that during dehydration process there are hardly any changes in the surface area and in the density.

D. X-ray diffraction sutdies: The results confirm the conclusions given above but they would require separate discussion /5/.

CONCLUSIONS

The investigations presented above indicate that not diffusion of water molecules from the lattice and the reaction at the phase boundary are responsible for the rate of dehydration of $K_2Ca(SO_4)_2.H_2O$ but the formation of a new phase (anhydrous product) and the decay of the original solid which occur simultaneously. In other words it is clear that the dehydration of syngenite is strongly topotactic.

REFERENCES

1 J. E. Conley and E. P. Partridge, Bulletin 459, Washington 1944.

2 K. Wieczorek-Ciurowa, Ph.D. Thesis (in Polish), Technical University of Cracow, Cracow 1976.

3 J. Dankiewicz and K. Wieczorek-Ciurowa, J. Therm. Anal., 13 (1978) 543; ibid. 15 (1979) 11.

4 J. Paulik and F. Paulik, Simultaneous Thermoanalytical Examinations by Means of the Derivatograph, in Wilson-Wilson's Comprehensive Analytical Chemistry, Ed. G. Svehla, vol. XII, adv. Ed. W. W. Wendlandt, Elsevier Sci., Publ. Comp., Amsterdam 1981.

5 K. Wieczorek-Ciurowa, in preparation.