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THERMOANALYTICAL STUDY OF $(NH_4)_2Cd_2(SO_4)_3$,INTERMEDIATE COMPOUND IN THE HEATING OF THE MIXTURE $(NH_4)_2SO_4/CdCO_3$ 1/1 M.

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ABSTRACT

In a previous study about the mechanism of the formation of $CdSO_4$ starting from mechanical mixtures $(NH_4)_2SO_4/CdCO_3$ 1/1 M (1), we identified $(NH_4)_2Cd_2(SO_4)_3$ as intermediate compound,whose thermal behaviour we have studied.

Prymova et al.(2),mention the compound $NH_4H(SO_4)_2$,stable between 350-450ºC,as product of the decomposition of the double sulphate $(NH_4)_2Cd_2(SO_4)_3$.However ,we have not been able to isolate any intermediate compound during the study of this dissociation.

By X-ray analysis of the interval 350-450ºC,we identified the diffractions of $(NH_4)_2Cd_2(SO_4)_3$,$CdSO_4$ and $(NH_4)_2SO_4$ with several new lines whose identification is being studied.About 400ºC,these lines,that could correspond to a product of the $(NH_4)_2Cd_2(SO_4)_3$ decomposition,are the dominant of the diffractogram.

The study is carried out by TG,DTA,X-ray powder diffraction and IR spectroscopy.

INTRODUCTION

In a previous study about the mechanism of the formation of $CdSO_4$ starting from mechanical mixtures $(NH_4)_2SO_4/CdCO_3$ 1/1 M (1), we identified an intermediate compound:$(NH_4)_2Cd_2(SO_4)_3$.Its thermal behaviour is the subject matter of this communication.

Since isolating this compound is not possible during the course of the indicated reaction,we have synthesized it in the laboratory.

In (1) we showed that the $(NH_4)_2Cd_2(SO_4)_3$ dissociation takes place without the formation of any isolable compound,being necessary the total decomposition of the double sulphate in order that the solid phase is $CdSO_4$.

EXPERIMENTAL PROCEDURES

Samples.$(NH_4)_2Cd_2(SO_4)_3$,prepared by evaporation to dryness on hot plate of a disolution containing $(NH_4)_2SO_4$ and anhydrous $CdSO_4$ in rate 1/2.The X-ray powder diffractograms of the evaporation residua are very complex:together with the searched double salt,we find $(NH_4)_2Cd(SO_4)_2$.6 H_2O and a variable number of lines

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not identified.

Heating the residua at temperatures between 150 and 250ºC,we have obtained pure $(NH_4)_2Cd_2(SO_4)_3$.

Techniques. Thermogravimetry.Chevenard thermobalance,model 93 from Adamel.Photographic register.Differential Thermal Analysis. DTA apparatus constructed in the laboratory.Sintered alumina specimen holder.Chromel/Alumel differential thermocouple.Graphic recording Metrohm Labograph E478 .X-ray powder diffraction:Siemens D-500 diffractometer,equipped with K805 generator,graphite monochromater and Cu $K\alpha_1$ radiation.Infrared spectroscopy.Perkin Elmer 599 B instrument.KBr tablets.0,3% sample concentration.

RESULTS AND DISCUSSION

In the thermogravimetric study we used two heating rates: 300 and 150ºC/hour.The sample weight was 210,0 mg.The TG curve(fig.1, curve a)) has not sudden changes at both rates.The interval of decomposition is 220-440ºC(300ºC/h.) or 175-430ºC(150ºC/h.)

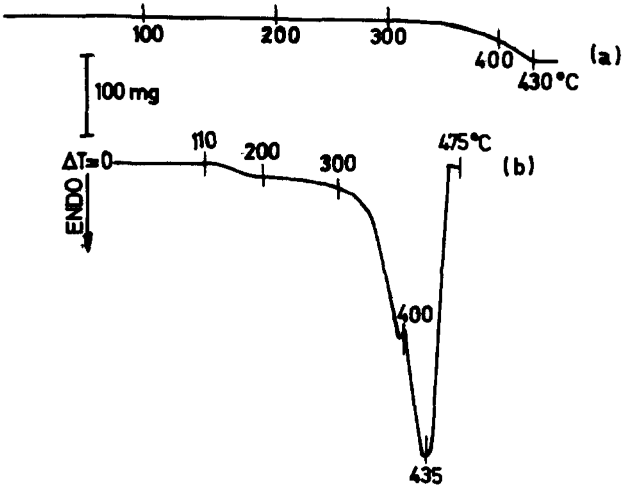

Figure 1.-TG and DTA curves at 150ºC/hour:curve a)TG, curve b)DTA

This interval has been analyzed by X-rays and IR spectroscopy at different temperatures between 175 and 500ºC.In the figure 2 we represent the IR spectra of the samples taken at 175,350,375, 400 and 500ºC.We only may observe the progressive decrease of the band of NH_4^+(A) and the band (B) of $(NH_4)_2Cd_2(SO_4)_3$ and the appearance of the band (C) belonging to $CdSO_4$.

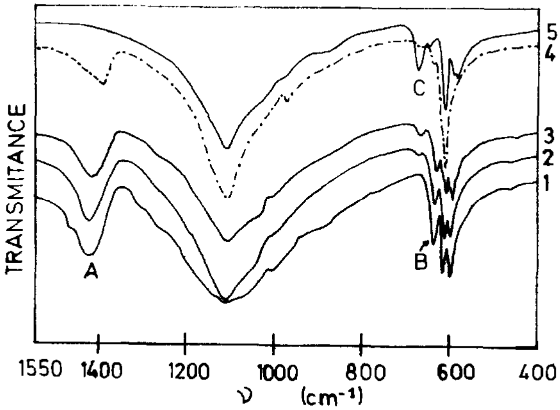

Figure 2.- IR spectra of samples taken at:1)175,2)350,3)375, 4)400,5)500ºC in the TG curve at 150ªC/hour.

In the X-ray diffractograms of the samples at 350,375 and 400ºC,we identified the double sulphate,$CdSO_4$,$(NH_4)_2SO_4$ and the same new lines that we found in (1) and in the residua of evaporation $(NH_4)_2SO_4$-$CdSO_4$ 1-2.

The total weight loss coincides with the loss associated to the formation of $CdSO_4$ starting from $(NH_4)_2Cd_2(SO_4)_3$(24,07%).The X-ray diffractogram of the residuum at 500ºC corresponds to anhydrous $CdSO_4$.

We have used for DTA slow heating rates,150 and 50ºC/h.,in order to separate all the possible consecutive processes.

In the figure 1,curve b),there is a little peak at 400ºC which is not possible to separate from the great peak of decomposition, even using slower heating rates.

The X-ray diffractograms and IR spectra of samples taken at predeterminated points of the DTA curves:385,400 and 410ºC(150ºC/hour) and 290,360,380 and 410ºC(50ªC/h.),do not provide any new data with respect to the results obtained from samples taken at TG curve.Together with the diffractograms of the three components mentioned before,the same new lines appear,which are the more intense of the diagram in the residuum at 400ºC(heating rate 150ºC/hour).

We emphasize that the double sulphate is always present in the whole interval of reaction, fact that indicates that its decomposition has not an isolable intermediate stage in our conditions of work.

Also, all the analyzed residua evolve with the time in the same way. Their new X-ray powder diffractions correspond to the hydrate $CdSO_4 \cdot H_2O$ and $(NH_4)_2Cd_2(SO_4)_3$. Theretore, the new lines and $(NH_4)_2SO_4$ disappear and $CdSO_4$ gets hydrated.

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