MECHANISM OF THE DEHYDRATION
OF CoHPO₄·1.5H₂O

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(Received June 26, 1987)

The dehydration of CoHPO₄·1.5H₂O has been followed by means of thermal analyses at quasi isothermal-isobaric conditions. The intermediates and products prepared in the course of the TA and by calcination of the starting hydrogen phosphate in electric ovens at various temperatures have been analyzed and identified by means of thin-layer chromatography, IR spectroscopy, X-ray diffraction analysis and electron microscopy.

Condensed phosphates of divalent metals are thermally and chemically stable compounds [1, 2] whose properties allow their applications in two areas: as long-acting microelement fertilizers and as special inorganic pigments. The cobalt-containing products possess distinct colour hues [3, 4] as well as certain anticorrosion effects.

The condensed phosphates can be prepared by calcination of hydrogen or dihydrogen phosphates of the respective metals or from mixtures containing the corresponding amounts of the phosphoric and the divalent components [1]. The formation of dicobalt diphosphate (Co₂P₂O₇) by calcination of cobalt hydrogen phosphate (CoHPO₄·1.5H₂O) was given considerable attention by some authors [5–8]. The papers, however, are not quite concordant with respect to the formation of the condensation intermediates [5, 6, 8] and to mutual interconversions of the two diphosphate modifications [7, 8, 17]. Structure [9], magnetic properties [10] and application of dicobalt phosphate in the above-mentioned areas [8] were also studied.

On the basis of the results [11] of thermal decompositions of Ca²⁺ and Mg²⁺ hydrogen phosphates carried out by means of the thermogravimetric method at quasi isothermal-isobaric conditions [12, 13] it was presumed that also in the case of
CoHPO$_4$·1.5H$_2$O it would be possible to apply the same method to complete the picture of the course of the respective condensation reactions. The present paper gives an account of the experiments carried out in this respect.

**Experimental**

Pure cobalt(II) hydrogen phosphate in the form of pink-violet fine crystals was prepared [11] by the reaction of cobalt(II) hydroxyde-carbonate with trihydrogenphosphoric acid. Its X-ray diffraction analysis confirmed a layer structure of the crystalline substance whose typical, most intensive line lies at $d = 7.5 \cdot 10^{-10}$ m. It contained the cobalt(II) and phosphoric components in the molar ratio CoO/P$_2$O$_5$ = 1.997, and the water content found by calculation was 14.9% which corresponded to 1.5 molecule of crystal water. The thermal analyses carried out at quasi isothermal–isobaric conditions were performed by means of Derivatograph Q–1500 D apparatus (Hungarian Optical Works MOM Budapest). The decomposition rate was 0.5 mg min$^{-1}$ (calculated for 100 mg total weight change). The sample weight was 350 mg, and the examination was carried out in the presence of air.

Various types of platinum crucibles [12, 13] (Fig. 1) were used to the measurements: A) multiplate sample holder, B) open crucible, C) crucible with a lid and D) a labyrinth crucible. The last arrangement (D) holds back the water vapour released by calcination up to the point where its partial pressure in the inside of the crucible reaches 100 kPa (quasi isobaric conditions) [12, 13]. In the case of the

![Diagram showing different types of sample holders](image)

**Fig. 1** Thermogravimetric curves traced under quasi isothermal and quasi isobaric conditions by using different kinds of sample holder

*J. Thermal Anal. 34, 1988*