MAGNESIUM PHOSPHATE

Part VI.—Study of X-ray Powder Diffraction, IR Absorption and Thermal Decomposition of the Compounds $MgHPO_4.3H_2O$, $MgHPO_4$ and $Mg_2P_2O_7$

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X-ray powder diffraction data of $MgHPO_4.3H_2O$ have been recorded at room temperature (26°C). Its IR spectrum has been recorded and studied in detail. Differential thermal analysis of the compound has been made. The compound $MgHPO_4$ is amorphous to X-rays; its IR spectrum has been studied. IR spectrum of the compound $Mg_2P_2O_7$ has also been studied.

Many authors[1] described a few methods for preparing the compound $MgHPO_4. 3H_2O$. During this work the compound has been prepared and studied in the course of preparing anhydrous magnesium pyrophosphate which was used as a reagent during the investigation of the systems MgO–P_2O_5 and MgO–P_2O_5–Cr_2O_3. In the same time the compounds $MgHPO$ and $Mg_2P_2O_7$ have also been studied.

Experimental

Preparation.—The compound $MgHPO_4.3H_2O$ was obtained by heating $MgHPO_4.7H_2O$ at 100°C for a few minutes. On standing at room temperature for two to three days, $MgHPO_4.7H_2O$ spontaneously decomposes to $MgHPO_4.3H_2O$. The substance was also obtained as colourless hard crystals by dissolving anhydrous magnesium orthophosphate, $Mg_3(PO_4)_2$, or $MgHPO_4.7H_2O$ in concentrated acetic acid. $MgHPO_4.3H_2O$ crystalizes out from a saturated solution of $Mg_3(PO_4)_2$ or $MgHPO_4.7H_2O$ in acetic acid within a few hours at room temperature. The crystals are insoluble in water. The compounds $MgHPO_4$ and $Mg_2P_2O_7$ were obtained by heating $MgHPO_4.3H_2O$ at 213°C for 30 min and at 656°C for 1 hr respectively.

X-ray, IR and differential thermal analyses of all the three compounds were made by the methods described in Part V[2] of the paper of this series. Density of the substances were also measured by the methods mentioned in the same paper.

Results and Discussions

The results of chemical analyses of the above compounds have been shown in Table 1. The analytical results are in good agreement, within the experimental error, with those calculated on the basis of the chemical formulas $MgHPO_4.3H_2O$, $MgHPO_4$ and $Mg_2P_2O_7$. This shows that the compounds obtained are pure.

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The compound $MgHPO_4.3H_2O$ is finely crystalline to X-rays. Its X-ray powder diffraction data have been shown in Table 2. The data

TABLE 1.—CHEMICAL ANALYSES OF THE ABOVE SUBSTANCES.

Substances	Found (%)			Calculated (%)		
	MgO	P_2O_5	Water	MgO	P_2O_5	Water
$MgHPO_4.3H_2O$	22.99	40.60	36.42	23.11	40.67	36.22
$MgHPO_4$	33.50	58.96	7.55	33.52	59.00	7.48
$Mg_2P_2O_7$	36.05	63.90		36.22	63.78	

TABLE 2.—X-RAY POWDER DIFFRACTION FOR THE COMPOUND $MgHPO_4.3H_2O$.

I				II			
$d\,Å$	I/I_1	$d\,Å$	I/I_1	$d\,Å$	I/I_1	$d\,Å$	I/I_1
8.0400	5	2.4330	3	1.6696	3	5.9000	40
5.9250	75	2.4080	6	1.6584	4	5.3000	20
5.3560	79	2.3920	9	1.6420	3	4.7000	40
5.0960	3	2.3560	10	1.6180	1	4.1500	24
4.7200	100	2.3010	2	1.6000	3	3.6400	8
4.6060	17	2.2760	1	1.5890	4	3.4500	100
4.4960	18	2.2015	7	1.5656	3	3.0500	80
4.1420	19	2.1760	4	1.4960	2	2.8000	32
3.6920	6	2.1400	3	1.4650	1	2.7100	24
3.6380	8	2.0920	4	1.4456	2	2.5700	32
3.5700	6	2.0760	3	1.4162	3	2.3900	24
3.4730	94	2.0580	3	1.4060	1	2.2000	12
3.1860	15	2.0450	6	1.3894	2	2.0500	12
3.0800	69	1.9800	3	1.3776	1	1.9700	4
3.0450	62	1.9710	2	1.3322	2	1.9200	16
2.9740	1	1.9330	14	1.3275	1	1.8700	8
2.8980	16	1.8952	2	1.3187	2	1.7900	4
2.7970	25	1.8880	4	1.2860	1	1.7500	4
2.7220	26	1.8714	4	1.2606	2	1.6600	8
2.6710	3	1.7990	4	1.2520	2	1.5900	8
2.5810	41	1.7872	1	1.2356	1	1.4900	4
2.5530	1	1.7582	4	1.2190	1	1.4100	8
2.5320	8	1.7230	3	1.2093	1	1.3800	4
2.5020	4	1.7010	1	1.1850	1	1.3300	4
2.4780	2	1.6820	7	1.1493	1		

Fig. 1.—IR spectra for the compounds Mg HPO$_4$. 3H$_2$O, Mg HPO$_4$ and Mg$_2$ P$_2$O$_7$.

published previouly[3] have been quoted here for easy comparision. When the two data are compared it is seen that in the case of the published data some of the d-values are missing. Though it is not mentioned in the literature, it seems that these data were calculated from the X-ray powder photograph and in that case it is very much possible to miss diffraction lines having very low intensity. Otherwise improved X-ray powder diffractometer may be the cause of recording more diffraction peaks during the present work. The compound MgHPO$_4$ is amorphous to X-rays. Anhydrous magnesium pyrophosphate is finely crystalline to X-rays. Its X-ray powder diffraction data have been found to be identical to those published earlier.[4]

The IR spectra of the three compounds have been shown in Fig. 1. The IR spectrum (Fig. 1a) of MgHPO$_4$.3H$_2$O contains one valley from 3700 cm^{-1} to 3200 cm^{-1} and in this valley there are several well-defined absorption bands; the band at 3280 cm^{-1} is due to O—H stretching vibration and the other bands are due to some other mode of O—H vibration, this suggests that there is extensive hydrogen bonding. There are two weak absorption bands at 2840 cm^{-1} and 2880 cm^{-1} respectively; one of them seems to be due to P—O—H stretching. The absorption band due to P—H stretching is at 2480 cm^{-1}. There is one absorption band at 2400 cm^{-1} which could not be accounted for. From 1750 cm^{-1} to 1600 cm^{-1} there is one valley and it contains two absorption bands; the band at 1655 cm^{-1} is due to O—H bending but that at 1705 cm^{-1} could not be accounted for. There are several sharp and strong

absorption bands in the region 1300 cm^{-1}–100 cm^{-1}. The band at 1240 cm^{-1} seems to be due to P=O stretching and that at 1170 cm^{-1} could not be accounted for that at 1065 cm^{-1} may be due to P—O ionic stretching while that at 1025 cm^{-1} seems to be due to P—O—H deformation mode. There is one strong absorption band at 900 cm^{-1}, it seems to be due to P—O—H bending. The absorption bands in the region 800 cm^{-1}–400 cm^{-1} are not well-defined. The IR spectrum (Fig. 1b) of MgHPO$_4$ contains no well-defined absorption band but some valley only; this is the characteristics of an amorphous compound.

In the IR spectrum (Fig. 1c) of Mg$_2$P$_2$O$_7$ all the absorption bands lie in the region 1250 cm^{-1} to 400 cm^{-1}. These bands are mainly due to the ion:

$$O=\overset{\displaystyle O^-}{\underset{\displaystyle O^-}{P}}-O-\overset{\displaystyle O^-}{\underset{\displaystyle O^-}{P}}=O$$
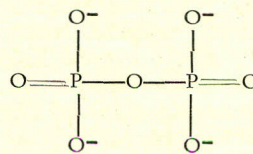
The absorption bands in the region 1250 cm^{-1}–1060 cm^{-1} are strong but not well-defined; and these bands are due to P=O bonding. The absorption band at 1055 cm^{-1} is very sharp and well-defined, it is due to P—O ionic stretching. The band at 980 cm^{-1} is strong but broad and ill-defined, it seems to be due to P—O—P stretching. The absorption band at 740 cm^{-1} is very well-defined and sharp also; this band arises from the harmonics of P—O—P bending. There are three more bands at 590, 555 and 510 cm^{-1} respectively
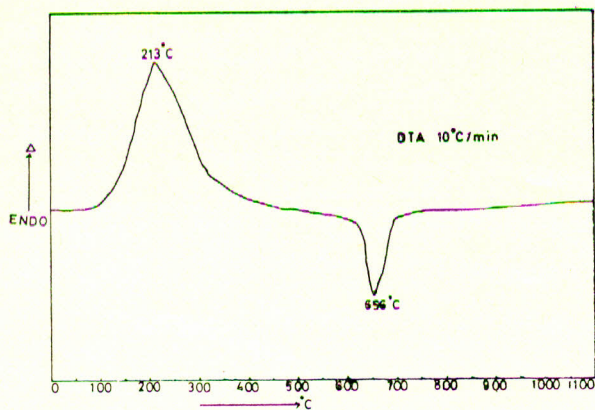
Fig. 2.—Differential thermal analysis curve for the compound Mg HPO₄3H₂O.

and they may arise from O—Mg—O stretching and bending.

The compound $MgHPO_4.3H_2O$ is orthorhombic dipyramidal[5] with a–b–c = 0.955:1:0.936; n_x = 1.514, n_y = 1.517, n_z = 1.533 and $n_z - n_x$ = 0.019. The density of the substance has been found to be 2.10 g/cm³ at 23°C while the density of $MgHPO_4$ at the same temperature has been found to be 2.45 g/cm³.

Differential Thermal Analysis of $MgHPO_4.3H_2O$.— The curve (Fig. 2) of differential thermal analysis shows that $MgHPO_4.3H_2O$ decomposes to $MgHPO_4$ at 213°C and the last molecule of water is removed at 656°C, forming crystalline magnesium pyrophosphate. The differential thermal analysis curve[6] of $MgHPO_4.7H_2O$ has shown that in the case of $MgHPO_4.7H_2O$, formation of $MgHPO_4$ and $Mg_2P_2O_7$ has been occurred at 205 and 612°C respectively. Hence the arrangement of water of crystalization is not same in $MgHPO_4.7H_2O$ and $MgHPO_4.3H_2O$, although on dehydration both of them give same compounds, namely $MgHPO_4$ and $Mg_2P_2O_7$. IR analyses also suggest that in $MgHPO_4.7H_2O$ and $MgHPO_4.3H_2O$ water molecules are arranged in different way. Structure determination by single crystal X-ray diffraction method may give us the real picture.

Differential Thermal Analysis of $Mg_2P_2O_7$.—This compound transforms from the alpha* to beta form at 70°C ($\pm2°$C). This change was also observed by Roy, Middleswarth and Hummel.[7] The phase transformation is not permanent, on cooling the beta form reverts at once to the alpha form. Further heating up to 1100°C shows no phase change. It melts congruently at 1383°C but forms no glass, even on rapid cooling to room temperature.

The compound $\alpha\text{-}Mg_2P_2O_7$ is monoclinic with the following lattice constants:[8] a = 6.58 Å,

b = 8.28 Å, c = 9.08 Å, β = 104° 11', z = 4. The density of the substance was not mentioned in the literature. The value calculated from the above lattice constants is 3.428 g/cm³. The crystal structure of the $\beta\text{-}Mg_2P_2O_7$ has been determined by Lukas Zeariez.[9] He has found $\beta\text{-}Mg_2P_2O_7$ to be isostructural with thortueitite, $Se_2Si_2O_7$, and the following lattice constants have been found: a = 6.49 Å, b = 8.28 Å, c = 4.51 Å, β = 104°5', z (number of molecules in unit cell) = 2 and D (density) = 3.156 g/cm³.

When the crystallographic data of the alpha and the beta forms of $Mg_2P_2O_7$ are compared it is found that both the forms are monoclinic and the unit cells b is same while the edge a is slightly different, 0.09 Å higher in the case of the alpha form. But the edge c is reduced to nearly half in the beta form. The angle β (angle between the edge a and c) has widen in the alpha form. As a result the volume of the unit cell of the alpha form has increased, and the number of molecules in the unit cell of the beta form has reduced to 2, accordingly its density has also been reduced. All these caused by the slight rise of temperature only; so the structure of the alpha form is susceptible to temperature and at elevated temperature the structure of the beta form is very strong as shown by the high fusion point (1383° °C) of the compound. But energetically the beta form is not stable, this is why $\beta\text{-}Mg_2P_2O_7$ reverts at once to $\alpha\text{-}Mg_2P_2O_7$ on cooling.

References

1. J.W. Mellor, *Comprehensive Treaties on Inorganic and Theoretical Chemistry* (1952), p. 390.
2. S. Ahmed, Sci. Researches (in press).
3. A.S.T.M. Index Card No. 1–0601.
4. A.S.T.M. Index Card No. 8–38.
5. A.N. Winchell and H. Winchell, *The Microscopical Characters of Artificial Solid Substances: Optical Properties of Artificial Minerals* (1964), p. 198.
6. S. Ahmed, Sci. Researches (in press)
7. R. Roy, E.T. Middleswarth and F.A. Hummel, Am. Mineralogist, **33**, 458 (1948).
8. A.S.T.M. Index Card No. 8–38.
9. K. Lukaszewicz, Roczniki Chem., **35**, 31 (1961).

*The form stable at the room temperature is termed as the α-form.