The "Overcondensation" of Phosphate Ions and the Formation of Conjugate Metal Oxide upon the Thermal Dehydration-condensation of Hydrogenorthophosphates

Hiroshi KAWAZOE,* Kazuo AMETANI,† Masahiko IMAI,† and Takafumi KANAZAWA

Department of Industrial Chemistry, Faculty of Technology, Tokyo Metropolitan University, Fukazawa, Setagaya-ku, Tokyo 158

†*Tokyo Metropolitan Isotope Research Center, Fukazawa, Setagaya-ku, Tokyo 158*

(Received September 19, 1977)

On the thermal reaction of H_3PO_4 or $NH_4H_2PO_4$ with metal salts, such as Na_2CO_3 or $Mg(OH)_2$, the "overcondensation" of the phosphate anions and the conjugate formation of metal oxide were observed. The "overcondensation" was defined as a formation reaction of the phosphate with a larger polymerization degree than that of the product to be expected from the [MO or M_2O]/[P_2O_5] mole ratio of the starting mixtures. The "overcondensed" tetrametaphosphate and the conjugate oxide, magnesium oxide, were detected on the thermal condensation of $MgHPO_4 \cdot 3H_2O$ and of a mixture of $NH_4H_2PO_4$ or H_3PO_4 and $Mg(OH)_2$. The "overcondensed" tripoly- and trimeta-phosphate were found in the course of the formation reaction of Na pyrophosphate from a mixture of Na_2CO_3 and $NH_4H_2PO_4$.

A free electron was found to be trapped in a lattice defect formed during the dehydration-condensation (abbreviated as D-C) reaction of hydrated hydrogenorthophosphates.[1)] Especially, on the thermal condensation of $MgHPO_4 \cdot 3H_2O$ (DMP3), an ESR center which may be assigned to the trapped electron at an oxygen vacancy in MgO (the so-called F center) was detected. The magnesium oxide was considered to arise upon the reaction. The formation of MgO must be accompanied by the formation of the condensed phosphate, which has a greater polymerization degree than that of pyrophosphate. Therefore, it may be supposed that the thermal condensation reaction progresses through the separation of metal oxide and the "overcondensation" of phosphates. This "overcondensation" is defined as the formation reaction of the condensed phosphates with a larger polymerization degree than that of the product to be expected from the mole ratio of the starting sample, [MO or M_2O]/[P_2O_5].

It is the purpose of the present paper to examine whether or not a pair of conjugate reactions, the "overcondensation" of phosphates and the isolation of metal oxide, generally occurs on the D-C of orthophosphates. The condensation reactions of some sodium- and magnesium-orthophosphates to the respective pyrophosphates were done, and the "overcondensed" phosphates were identified by means of X-ray diffraction or ESR spectroscopy for irradiated samples. The formation of amorphous magnesium oxide was verified by using the ESR technique for the Mn(II)-doped samples.

Experimental

In order to obtain the intermediates in the reaction, a mixture of metal salt and phosphate or phosphoric acid was placed in a high-alumina crucible and heated in an electric furnace at several fixed temperatures. The thermal reactions for preparing the respective pyrophosphates were as follows:

$$2Na_2CO_3 + 2NH_4H_2PO_4 \longrightarrow Na_4P_2O_7 + 2NH_3 + 2CO_2 + 3H_2O$$

$$2Mg(OH)_2 + 2NH_4H_2PO_4 \longrightarrow Mg_2P_2O_7 + 2NH_3 + 5H_2O$$

$$2Mg(OH)_2 + 2H_3PO_4 \longrightarrow Mg_2P_2O_7 + 5H_2O$$

$$2MgHPO_4 \cdot 3H_2O \longrightarrow Mg_2P_2O_7 + 7H_2O.$$

All the chemicals used except DMP3 were guaranteed-grade reagents (Kanto Chemicals, Ltd.). The magnesium hydrogenphosphate trihydrate was produced by the reaction of $Mg(OH)_2$ with H_3PO_4 and was used as one of the starting samples for magnesium pyrophosphate (MP) preparation. The magnesium salts doped with Mn(II) were also prepared in order to examine whether or not the isolated MgO deposits in the course of the reaction. The manganese carbonate was dissolved in phosphoric acid or added to a mixture of powdered $Mg(OH)_2$ and $NH_4H_2PO_4$. The mole ratio of Mn/Mg was 1×10^{-4}.

The measurement of the X-ray diffraction were made for the powdered samples to check changes in the structure of the phosphates during the thermal reaction.

The measurements of the ESR absorption were carried out for the γ-irradiated specimens (^{60}Co source, for two hours at a dose rate of 0.5 Mrad/h) and Mn(II)-doped samples on a JEOL JES-PE-3X ESR spectrometer, mainly at room temperature.

Results and Discussion

"Overcondensed" Phosphates Detected by the X-Ray Powder Diffraction Method. Figure 1 shows the X-ray diffraction patterns of the specimens obtained by a thermal treatment of a mixture of Na_2CO_3 and $NH_4H_2PO_4$. The pattern for the material heated at 300 °C (d) was attributed to that of sodium tripolyphosphate (Form II).[2)] A successive heating up to 520 °C (b) resulted in the crystallization of sodium trimetaphosphate[3)] in addition to tripolyphosphate. The degradation of the "overcondensed" phosphates, *i.e.*, tripoly- and trimeta-phosphates, into sodium pyrophosphate occurred above 620 °C (a).[4)]

The X-ray diffraction patterns for the heat-treated magnesium salts are shown in Fig. 2. As may be seen in the figure, the diffraction patterns were identical for the two cases starting from different phosphates, *i.e.*, ammonium dihydrogenphosphate and phosphoric acid. The crystalline material formed by heating at 730 °C (b, e) was identified as not magnesium pyrophosphate, but magnesium tetrametaphosphate.[5,6)] In this stage

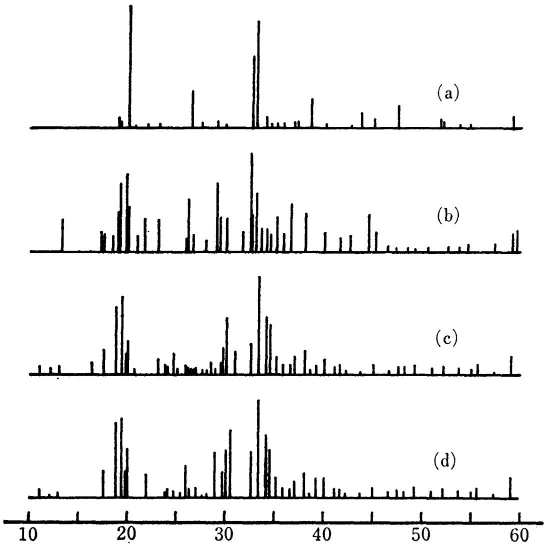

Fig. 1. X-Ray diffraction patterns of the mixture of Na_2CO_3 and $NH_4H_2PO_4$ (1: 1 in mole ratio) heated at a: 620, b: 520, c: 400, and d: 300 °C.

of the reaction, no other crystalline phosphates were found. The tetrametaphosphate changed into MP at higher temperatures (a, c, d).[7] The results are summarized in Table 1. It may be inferred from these results that the formation of "overcondensed" phosphates with a larger polymerization degree than that of pyrophosphate takes place in the course of the condensation of orthophosphates. The condensation through the formation of the "overcondensed" phosphates must be the predominant path, since the crystallinity of the samples obtained by heating at lower temperatures was quite high (in the order of 10%) and no detectable signal of pyrophosphate formation was seen in the diffraction patterns. It may be noted that the formation of the oxides in the heated samples was not detected by the X-ray method because of the relatively low crystallinity of MgO and the unstability of Na_2O.

Detection of the Amorphous "Overcondensed" Phosphates and Amorphous Magnesium Oxide by the ESR of Mn(II). We made a prediction that the "overcondensation" is accompanied by the isolation of metal oxide. The utilization of ESR of incorporated Mn(II) made it possible to examine the formation of amorphous magnesium oxide. The ESR spectra for Mn(II)-doped samples are shown in Fig. 3. Only the fine-structure component responsible for the $M=1/2 \leftrightarrow -1/2$ transition with six hyperfine structure lines produced by ^{55}Mn ($I=5/2$) had a detectable strength of the signals. The (a) and (c) spectra were taken as the references; (a) was the well-known pattern of Mn(II) in the MgO host crystal,[8] while (c) was the absorption due to Mn(II) in polycrystalline magnesium tetrametaphosphate.[9] The (b) pattern, taken from the specimen heated at 730 °C, may be regarded as a close superposition of the other two spectra, (a) and (c). An extra peak found near $g=2.002$ is attributable to the electron trapped in a lattice defect.[1] It may, therefore, be

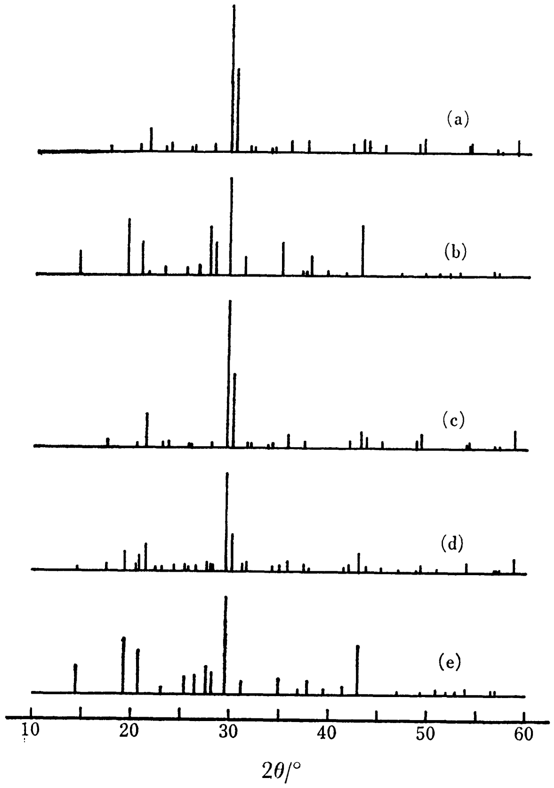

Fig. 2. X-Ray diffraction patterns of the mixtures of $Mg(OH)_2$ and a phosphate (MgO/P_2O_5 mole ratio=2) heated at a: 1075 °C for 2 h, b: 730 °C for 15 h, c: 1075 °C for 2 h, d: 920 °C for 2 h, and e: 730 °C for 15 h. Orthophosphoric acid was used as a starting reagent for a and b, whereas $NH_4H_2PO_4$ was utilized for c, d, and e.

TABLE 1. CRYSTALLINE PHASES IDENTIFIED IN SAMPLES HEAT-TREATED UNDER VARIOUS CONDITIONS

$2Na_2CO_3+2NH_4H_2PO_4$[a]		$2Mg(OH)_2+2NH_4H_2PO_4$ or $2H_3PO_4$[a]		$MgHPO_4\cdot 3H_2O$
Heating condition	Identified crystal	Heating condition	Identified crystal	Identified crystal
300 °C 15 h	$Na_5P_3O_{10}$	730 °C 15 h	$Mg_2P_4O_{12}$	$Mg_2P_2O_7$
400 °C 2 h	$Na_5P_3O_{10}$	920 °C 2 h	$Mg_2P_2O_7$	$Mg_2P_2O_7$
520 °C 2 h	$Na_5P_3O_{10}$ $(NaPO_3)_3$	1075 °C 2 h	$Mg_2P_2O_7$	$Mg_2P_2O_7$
620 °C 2 h	$Na_4P_2O_7$			

a) Samples obtained by mixing the reagents shown in this table.

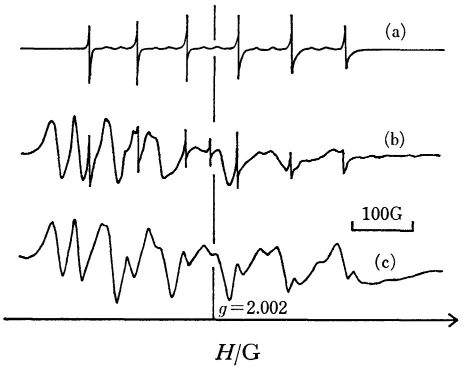

Fig. 3. ESR spectra of Mn(II) in various host crystals. a: In MgO, b: in the specimen obtained by heating 1: 1 mixture of $Mg(OH)_2$ and $NH_4H_2PO_4$ at 730 °C and c: in $Mg_2P_4O_{12}$.

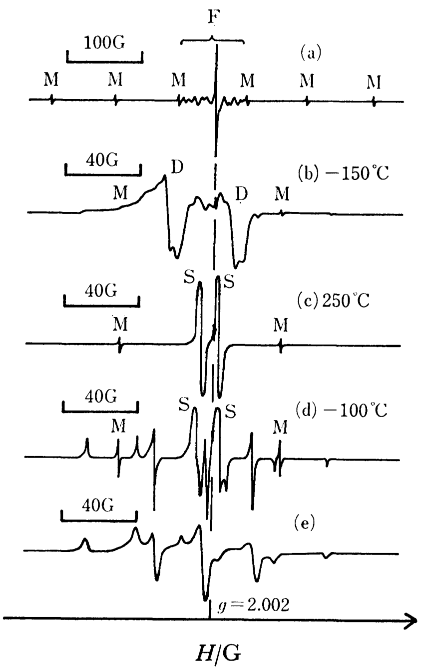

Fig. 4. ESR spectra for $MgHPO_4\cdot 3H_2O$. a: Mn(II)-doped sample heated at 700 °C. b, c, d: Specimens obtained by heating DMP3 doped with Mn(II) at 730 °C for 15 h and by irradiating with γ-ray at a liquid nitrogen temperature. The spectrum b was recorded without intervening warming up to room temperature and c was measured at 250 °C. The spectrum d was obtained at −100 °C after bleaching out (at 300 °C) the intense signals arising from PO_4^{2-} radicals. e: γ-irradiated $Mg_2P_4O_{12}$ obtained by heating 1: 1 mixture of $NH_4H_2PO_4$ and $Mg(OH)_2$ at 1100 °C. Signal gain for c and d is ten times larger than that for b.

concluded that the "overcondensation" of phosphate ions and the isolation of magnesium oxide proceed simultaneously in the course of the D-C reactions of orthophosphate with magnesium salt.

No trace of the "overcondensation" of phosphates or of the isolation of MgO crystals was seen by X-ray diffraction when DMP3 was used as the starting sample. The process of the D-C reaction of DMP3 to MP is well established:[10]

$$\mathrm{MgHPO_4\cdot 3H_2O} \xrightarrow[-3\mathrm{H_2O}]{1\quad 180\ ^\circ\mathrm{C}} \text{amorph. } \mathrm{MgHPO_4} \xrightarrow[-\mathrm{H_2O}]{2\quad \text{above } 300\ ^\circ\mathrm{C}}$$

$$\text{amorph. } \mathrm{Mg_2P_2O_7} \xrightarrow{3\quad \text{above } 450\ ^\circ\mathrm{C}} \text{cryst. } \mathrm{Mg_2P_2O_7}.^{11)}$$

In the above reaction, the conversion to crystalline MP is slow at temperatures lower than about 900 °C. If amorphous "overcondensed" phosphate forms competitively with amorphous MP in Stage 2, it is undetectable by X-ray diffraction. In order to confirm the formations of the "overcondensed" phosphate and its conjugate oxide, ESR measurements were carried out on Mn(II)-doped DMP3 heated at 700 °C for several hours, which was still gray-colored and which exhibited the weak X-ray diffraction characteristic of crystalline MP. The results are shown in Fig. 4(a). The signals represented as F may be attributable to the F center in magnesium oxide.[12] The peaks labelled by M may be interpreted as resulting from the Mn(II) in the MgO host lattice. This fact strongly supports the formation of the isolated magnesium oxide. The manganese ions, of course, occupy also the sites of Mg ions in the condensed phosphates. Thus, the absorption responsible for these Mn(II) ions would be expected to appear. However, the environment of Mn(II) ions was considered to be distorted or to be widely distributed in these amorphous phosphates, and the resultant absorption was too broad to be shown in the figure. The underlying vague absorption (not shown in the figure) was assigned to these manganese ions.

In order to detect the counterpart of the isolated MgO, that is, the "overcondensed" phosphates, the measurements of ESR absorption were made on γ-irradiated samples which had been obtained by heating DMP3 doped with Mn(II) at 730 °C for 15 h in order to bleach out the trapped electron. The representative spectra are shown in Fig. 4 (b, c, d). The (b) spectrum was recorded without intervening warming up to room temperature after irradiation at the temperature of liquid nitrogen and (c) was measured at 250 °C. The (d) spectrum was obtained at −100 °C after bleaching out (at 300 °C) the intense signals arising from PO_4^{2-} radicals. The intense doublet seen in the (b) pattern (labelled by D) is identified as the PO_4^{2-} radical.[13] At present, the nature of the radical responsible for the doublet, S, in the (c) pattern is not clear, but a little should be mentioned about this center. This absorption was found to arise generally by the irradiation to pyrophosphates and to be stable up to 300 °C. The remarkable peak of the trapped electron was also visible near the *g* value of a free electron. The (e) spectrum was recorded on the γ-irradiated specimen obtained by heating a 1: 1 mixture of $NH_4H_2PO_4$ and $Mg(OH)_2$ at 1100 °C. The crystalline component in this sample was magnesium tetrametaphosphate. This spectrum was attributed to the radical (U) formed by the irradiation to the tetrametaphosphate crystal or its glass.[14] The center was formed only in the irradiated tetrametaphosphate and was not detected in other related, irradiated magnesium phosphates. The spectrum broadened beyond detection at above 200 °C because of the relatively short relaxation time. Three types of

ESR centers are recognized in the (d) pattern. The first is the unknown center (the doublet, S), the second, the radical (U) in the tetrametaphosphate host lattice, and the last, Mn(II) in the MgO host matrix.

It may, therefore, be concluded that the "overcondensation" of phosphates and the counterpart isolation of MgO occur also in the course of the D-C reaction of DMP 3.

References

1) H. Kawazoe, M. Nishino, H. Hosono, K. Isozaki, K. Ametani, M. Imai, and T. Kanazawa, *Bull. Chem. Soc. Jpn.*, **51**, 2882 (1978).

2) ASTM X-Ray Powder Data File 11-652.

3) ASTM X-Ray Powder Data File 11-648.

4) ASTM X-Ray Powder Data File 10-187.

5) ASTM X-Ray Powder Data File 11-41.

6) A. G. Nord and K. B. Lindberg, *Acta Chem. Scand.*, **A29**, 1 (1975).

7) ASTM X-Ray Powder Data File 8-38.

8) W. Low, *Phys. Rev.*, **105**, 793 (1957).

9) H. Kawazoe, M. Nishino, M. Chikazawa, T. Umegaki, and T. Kanazawa, 36th National Meeting of the Chemical Society of Japan, Osaka, April 1977, Abstr. No. 2J25.

10) T. Kanazawa, *Kagaku No Ryoiki*, **24**, 222 (1970).

11) The second stage of the reaction could not be viewed as dehydration from the viewpoint of the microscopic mechanism of the reaction. This stage was found to proceed through the detachment of atomic hydrogen. This has been discussed in Ref. 1.

12) J. E. Wertz, P. Auzins, R. A. Weeks, and R. H. Silsbee, *Phys. Rev.*, **107**, 1535 (1957).

13) M. Miura and A. Hasegawa, *Bull. Chem. Soc. Jpn.*, **39**, 1432 (1966); S. Sabramanian, M. C. R. Symons, and H. W. Wardale, *J. Chem. Soc., A*, **1970**, 1239.

14) D. M. Yudin, A. V. Shendrik, M. L. Petrovskaya, and G. P. Nikolina, *Soviet Phys. Solid State*, **15**, 1754 (1974); *Fiz. Tverd. Tela.*, **15** 2636 (1973).