The Formation of Trapped Electrons upon the Thermal Dehydration-condensation of Hydrated Hydrogenorthophosphates

Hiroshi KAWAZOE,* Masaru NISHINO, Hideo HOSONO, Kei ISOZAKI, 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*

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Radical formation was found in the thermal dehydration-condensation process of hydrated hydrogenorthophosphates (HHP). It was considered that the intermediate radical reacted with lattice defects, thus resulting in the generation of trapped electrons. The gray coloration and the ESR sensitivity of the heated HHP were assigned to the formation of the trapped electron.

Some hydrated hydrogenorthophosphates (HHP), such as $MgHPO_4 \cdot 3H_2O$ (DMP3) and $Mg(H_2PO_4)_2 \cdot 2H_2O$, turn gray in the course of the thermal dehydration-condensation (D-C) reaction, resulting in a pyro- or meta-phosphate formation. These colored materials are bleached before the completion of the reaction; they change into white polycrystalline powders of pyro- or meta-phosphate. These facts suggest that a color center forms in the reaction process. In the present work, the nature of the color center was studied by means of ESR- and electronic-spectroscopies. The change in the concentration of the center with the reaction time was determined. The role of the center in the reaction was then discussed on the basis of these measurements.

Experimental

All the chemicals used here were guaranteed-grade reagents produced by Kanto Chemicals, Ltd. These reagents, *i.e.*, $MgHPO_4 \cdot 3H_2O$, $NaH_2PO_4 \cdot 2H_2O$, $Na_2HPO_4 \cdot 12H_2O$, $CaHPO_4 \cdot 2H_2O$, $Ca(H_2PO_4)_2 \cdot H_2O$, $KH_2PO_4 \cdot nH_2O$, and K_2HPO_4, were used as the starting samples without further purification. The $Mg(H_2PO_4)_2 \cdot 2H_2O$ sample was synthesized from MgO and H_3PO_4.[1]

Thermogravimetric and differential thermal analyses were made to determine the temperatures of dehydration and crystallization of their dehydrated phosphate samples.

Electron spin resonance measurements were carried out for the materials obtained by thermal treatment with varying temperatures and times for HHP. The spectra were recorded on a JEOL JES-PE spectrometer at an X band microwave frequency. The concentrations of an unpaired spin in the heated samples were measured by using a double-mode cavity, with a known amount of polycrystalline DPPH as a reference.

A visible-UV spectrum was taken on a Shimadzu UV-200 spectrometer for the colored HHP dissolved in a sodium metaphosphate glass matrix.

The crystallinities of heat-treated DMP3, *i.e.*, a fraction of the $Mg_2P_2O_7$ crystal, at 700 °C at various times were determined by comparing the X-ray diffraction intensity for the (022) of $Mg_2P_2O_7$ in the sample with that in the calibration curve. This curve was obtained from mixtures of crystalline $Mg_2P_2O_7$ and amorphous $MgHPO_4$ in various mixing ratios.

Results and Discussion

Nature of the ESR Center. The electron spin resonance spectra for the samples obtained by the thermal treatment of several HHP are shown in Fig. 1. The heating temperatures and times noted in the figure were the conditions under which the most intense absorptions were observed for the respective HHP. All HHP excepting for K_2HPO_4 showed ESR absorptions of a singlet type, no other signals were recognized. The features of the singlets were regarded as the same for all the samples, even though the absorption intensities for the respective phosphates were different from one another. Three common natures of the absorptions were recognized: the first, no hyperfine structure; the second, a line width of 1—2 G measured at a peak-to-peak width in the derivative curve, and the last, a nearly isotropic spectroscopic splitting tensor with a value equivalent to that of a free electron (g=2.002). In the

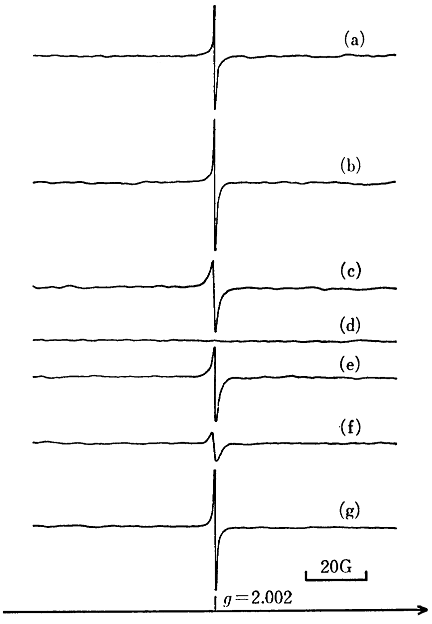


Fig. 1. ESR spectra for hydrated hydrogenorthophosphates heat-treated under the conditions shown below, a: $NaH_2PO_4 \cdot 2H_2O$, at 500 °C for 1 h, b: $Na_2HPO_4 \cdot 12H_2O$, at 500 °C for 1 h, c: $KH_2PO_4 \cdot nH_2O$, at 500 °C for 1 h, d: K_2HPO_4, at 200—800 °C for 0.5—10 h, e: $Ca(H_2PO_4)_2 \cdot H_2O$, at 400 °C for 1 h, f: $CaHPO_4 \cdot 2H_2O$, at 300 °C for 1 h, g: $Mg(H_2PO_4)_2 \cdot 2H_2O$, at 700 °C for 1 h. The spectra were recorded at 25 °C.

cases of $CaHPO_4 \cdot 2H_2O$, $KH_2PO_4 \cdot nH_2O$, and $Ca(H_2PO_4)_2 \cdot H_2O$, the $\boldsymbol{g}$ tensor was slightly anisotropic; *i.e.*, $g_\parallel = 2.0025$ and $g_\perp = 2.0023$. It should be noticed that K_2HPO_4 contains no water of crystallization. It may be expected, therefore, that lattice defects formed by the dehydration of HHP contribute to trapping the unpaired electron. Similar ESR centers were found in SiO_2, MgO, and CaS, all subjected to an explosive shock.²⁾ The color of these powdered materials was also gray.

We found that metaphosphate glasses are good trappers of these electrons. Sodium metaphosphate containing a small amount of HHP (1% in wt) was fused at 700 °C for 10 min and then quenched by using two plates of stainless steel. The glasses thus obtained were gray in color, but transparent to visible light. These glasses are suitable for the photo-bleaching and the measurement of an electronic spectrum. An electron spin resonance spectrum measured on the glass is shown in Fig. 2(b). The same singlet as that obtained by heating HHP (Fig. 1) reappeared. A unique difference between the spectrum of heated HHP (a) and that of HHP-doped metaphosphate glass (b) was a remarkable increase in the absorption intensity (in the order of 10^1—10^3) for the glass.

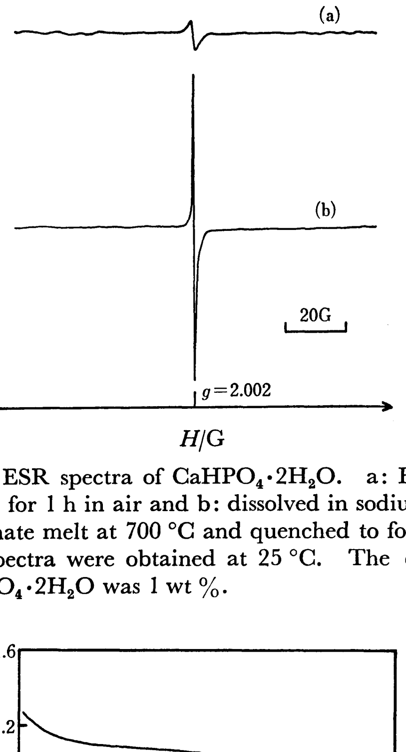


Fig. 2. ESR spectra of $CaHPO_4 \cdot 2H_2O$. a: Heated at 300 °C for 1 h in air and b: dissolved in sodium metaphosphate melt at 700 °C and quenched to form glass. The spectra were obtained at 25 °C. The concn of $CaHPO_4 \cdot 2H_2O$ was 1 wt %.

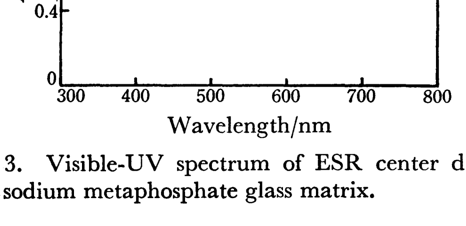


Fig. 3. Visible-UV spectrum of ESR center dissolved in sodium metaphosphate glass matrix.

Figure 3 shows the UV-visible spectrum for the glass containing DMP3. There was no characteristic peak, but a considerably intense absorption was seen over the range of wavelengths measured. If the lattice defect which is trapping an electron is assumed to make a three-dimensional, square-well potential, the difference between the energy levels for a trapped electron depends on the linear dimensions of the well. The size of the defects may be expected to be distributed in these amorphous matrices, and the absorption frequency may also be anticipated to have a wide distribution.

It is well known that DMP3 releases three water molecules at 180 °C and changes into $Mg_2P_2O_7$ gradually liberating one more water molecule by a condensation reaction between two $HOPO_3^{2-}$ ions at temperatures above 300 °C.³⁾ The process of the reaction should not, however, be viewed as so simple as is illustrated by the above scheme. In solid matrices the reaction does not always take place homogeneously; the extent of the reaction and the kind of the reaction products may be different for local sites and for sites in bulk specimens. For example, the condensation process of two $HOPO_3^{2-}$ ions is accompanied by the formation of the isolated amorphous MgO and "overcondensed" magnesium tetrametaphosphate.⁴⁾ The ESR spectrum obtained at 25 °C is displayed in Fig. 4 for the DMP3 sample, heated at gradually increasing temperatures with a small rate up to 700 °C. This spectrum was assigned to an F center in MgO.⁵⁾ It is expected that 53% of all magnesium-oxygen octahedra should have ^{24}Mg and ^{26}Mg ($I=0$), since the only abundant (10.05%) isotope with a nonzero nuclear spin is ^{25}Mg ($I=5/2$). One should see a single narrow line for an electron in a negative-ion vacancy with such an environment. There are also centers with one or two ^{25}Mg ions around one electron, and these should give a six- or an eleven-line hyperfine pattern centered upon the strong component. Such centers constitute 36 and 10% of the total number respectively. The contributions of those centers with 3, 4, and 5 ^{25}Mg neighbors can be neglected because of their small populations. For the unit intensity of the central line, one should have an intensity of 0.11 for the

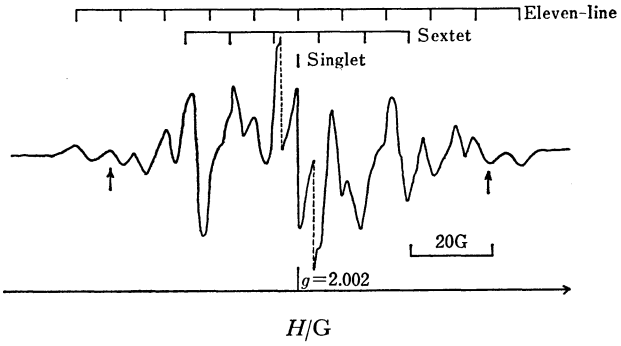


Fig. 4. ESR spectrum of DMP3 heated at gradually increasing temperatures up to 700 °C. Measurement was conducted at 25 °C. Signal gain for the central part is 1/10 of that for the outer parts. The expected locations of the singlet, sextet and eleven-line are also shown.

sextet and $0.0052n$ for the group of eleven lines, where $n=1, 2, 3, 4, 5, 6, 5, \cdots, 1$. In the figure, the absorptions responsible for the F center with 0, 1, and 2 ^{25}Mg are classified. A nerly isotropic hyperfine coupling tensor was assumed. The locations and intensities of the members of the sextet were in satisfactory agreement with the expection. However, the fourth and eighth members of the eleven lines diminished. This might be due to the interference of the two adjacent members of the more intense sextet. Furthermore, the locations of the second and tenth members were shifted, because the absorptions which are marked by arrows and which are not assignable overlapped with the member lines. The locations and intensities of the other members of the eleven lines were in fair agreement with the expectation. The hyperfine coupling constant was found to be 11 ± 1 G, which is larger than those ($A=5$ G and $A=3.5$ G) found in the single crystal of MgO.[5]

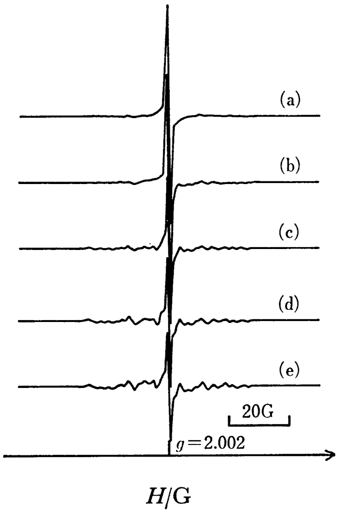


Fig. 5. ESR spectra for $MgHPO_4 \cdot 3H_2O$ heated at 700 °C for 1 h. The spectra were measured at a: −100 °C, b: −30 °C, c: 50 °C, d: 150 °C, and e: 245 °C.

The absorption profile shown in Fig. 4 changed gradually when the measuring temperature was varied. The spectra measured at different temperatures are illustrated in Fig. 5. The increase in the intensities of the sextet and eleven lines with an increase in the temperature was clearly recognized, whereas an inverse change was seen in the intensity of the central line. The change was found to be reversible. This fact suggests that an electron transfered from an F center in MgO to a lattice defect at lower temperatures, since the strong central line contains the contributions of the trapped electron in a lattice defect, besides that of the F center with no ^{25}Mg ion.

We may conclude here that a lattice defect formed in the reaction process acts as an electron-trapping site. The energy levels for the trapped electrons differ from site to site, corresponding to the distribution of the linear dimensions of the electron-trapping defects. Thus, the electronic spectrum for the electron has no peaks centered on a specific wavelength, but shows a rather wide absorption over the range of visible light.

Mechanism of Formation of Trapped Electrons. A major problem remaining is the mechanism of the dehydration-condensation reaction of HHP. In this article we wish to discuss the process by which an ESR center forms.

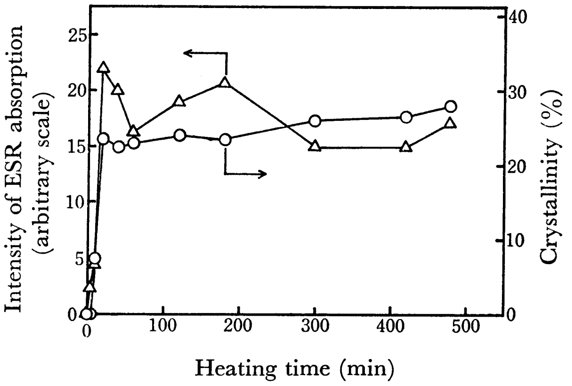
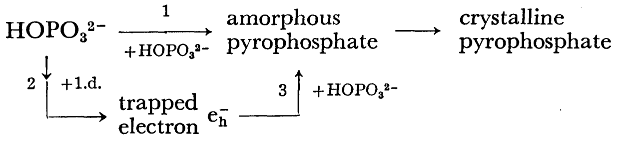


Fig. 6. Changes in ESR absorption intensity and crystallinity of $Mg_2P_2O_7$ with heating time. Specimens were $MgHPO_4 \cdot 3H_2O$ heated at 700 °C. The maximum concn of the trapped electron was ≈100 ppm.

This center emerged during the decomposition of $HOPO_3^{2-}$ ions. The intensities of ESR absorption and the crystallinities of magnesium pyrophosphate for DMP3 heated at 700 °C for various times are given in Fig. 6. The two properties changed similarly in the initial stage ($\lesssim$20 min), but they varied inversely afterwords. The initial variations in the two features are considered to be due to the release of water of crystallization and the successive decomposition of $HOPO_3^{2-}$ ions. The latter stage of the changes in the crystallinity is viewed as a rearrangement of the resultant amorphous magnesium pyrophosphate to form a crystalline lattice. The slow extinction of the trapped electron (20 min$\lesssim$) is probably due to the reaction of the electron with fragment ions. The value of the initial crystallinity (≈25%) depends on the experimental conditions. In this experiment, the samples initially equilibrated at room temperature were placed in an electric furnace maintained at 700 °C. The lattice structure of the HHP subjected to an abrupt temperature rise was destroyed by the vaporization of the water of crystallization. The resulting amorphous hydrogenorthophosphate, containing many cavities or voids among its constituent ions, was suitable for trapping an electron, but unsuitable for forming crystalline pyrophosphate. In the initial heating times, parallel changes in the two properties were recognized. The minimum temperature of heat-treatment generating the detectable ESR absorption for the respective HHP were also the lowest temperatures for the formation of the condensed phosphates. These two facts indicate that the trapped electron emerges during the decomposition of the $HOPO_3^{2-}$ ions.

It can be supposed that the D-C reaction between two $HOPO_3^{2-}$ ions proceeds at least partly through the formation of radicals at elevated temperatures, and that the trapped electron results from the reaction between the radical and the lattice defect. Distinct mechanisms have been proposed for the D-C reaction of $CaHPO_4 \cdot 2H_2O$ at higher temperatures and at lower temperatures.[6] No intermediate radical expected to be generated during the reaction, such as $H^\bullet$, ${}^{\circ}_{\bullet}OH$, ${}^{\circ}_{\bullet}OPO_3^{2-}$, and ${}^{\circ}_{\bullet}PO_3^{2-}$, was detected directly by the ESR method, but one of the derivatives of phosphine was found.[7] It may, therefore, be inferred that atomic hydrogen, $H^\bullet$, forms upon the reaction. One possible mechanism of forming a trapped electron is the process shown below:



Here, l.d. expresses a lattice defect. The 1 process was regarded as the direct radical condensation corresponding to the initial crystallinity shown in Fig. 6:

$$HOPO_3^{2-} \longrightarrow H^\bullet + {}^{\circ}_{\bullet}OPO_3^{2-}$$

$$H^\bullet + HOPO_3^{2-} + {}^{\circ}_{\bullet}OPO_3^{2-} \longrightarrow H_2O + P_2O_7^{4-}.$$

The 2 stage was viewed as the formation of the trapped electron:

$$H^\bullet + \text{l.d.} \longrightarrow e_h^- + H^+ \quad \text{or}$$

$$H^\bullet + HOPO_3^{2-} \longrightarrow H_2O + {}^{\circ}_{\bullet}PO_3^{2-}$$

$${}^{\circ}_{\bullet}PO_3^{2-} + \text{l.d.} \longrightarrow PO_3^- + e_h^-.$$

The 3 reaction was considered to be the extinction of the e_h^- of forming the $P_2O_7^{4-}$ ions:

$${}^{\circ}_{\bullet}OPO_3^{2-} + e_h^- + PO_3^- \longrightarrow P_2O_7^{4-}.$$

Other side reactions, such as the formation of a hydrogen molecule ($H^\bullet + H^\bullet \rightarrow H_2$) and the substitution of a hydrogen for an oxygen in a PO_4 tetrahedron, may be possible.

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