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SEPARATION OF THE RADIOLYSIS PRODUCTS OF HYPOPHOSPHITES

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SUMMARY

The formation of hypodiphosphite ($\overset{2}{P}-\overset{2}{P}$) as a hydrolytic product of the γ-ray decomposition products of ammonium hypophosphite was confirmed and the formation of $\overset{0}{P}-\overset{2}{P}$ was assumed from the anion-exchange chromatographic result. The half-life periods of these products were determined in 10^{-3} M hydrochloric acid, assuming that their reactions were first order.

INTRODUCTION

In the study of the γ-ray radiolysis of solid hypophosphite, it has been known that the radiolytic products and the rates of the decomposition of the ligand molecules in metal complexes are affected by the central metal ions and that alkali metal hypophosphite is comparatively sensitive to γ-ray irradiation[1]. Anselmo and Sanchez[2] reported briefly that two new active species attributed to N–P bonded compounds containing oxy-anions were observed in the study of ammonium hypophosphite irradiated with thermal neutrons. Kobayashi *et al.*[3] reported the existence of hypodiphosphite in neutron-irradiated sodium hypophosphite by means of paper chromatography. Our observation showed the formation of hypodiphosphite ion experimentally. Little is known about the chemical properties of this ion except for a report by Baudler *et al.*[4], although the existence of this ion has been known for many years. We have therefore investigated the chemical and chromatographic behaviour of this ion.

EXPERIMENTAL

Ammonium hypophosphite and sodium hypophosphite purified by recrystallization were used for the study of irradiation effect. Both samples, sealed in glass tubes in vacuum, were irradiated at a dose rate of $4.5 \cdot 10^5$ R h^{-1} at room temperature using 3500-Ci cobalt-60 at the γ-ray Irradiation Laboratory, Kyushu University. The total absorption dose was $1.0 \cdot 10^8$ rad and the irradiated samples were used for chemical separation immediately after the end of the irradiation. The irradiated samples (about 120 mg) were dissolved in 10 ml of 0.01 M hydrochloric acid and then diluted to 100 ml with water.

Anion-exchange chromatography was performed on a strongly basic anion exchanger [Bio-Rad AG 1-X8 (Cl^-), 100–200 mesh] column (66 × 1.54 cm I.D.). A gradient elution technique was applied by mixing 0.2 M sodium chloride into 750 ml of 0.075 M sodium chloride solution, all eluent solutions being buffered by adding 25 ml of 2 M ammonium acetate solution per litre of solution. The effluent was collected in 7-ml fractions with an automatic fraction collector of the weight type and an aliquot of each fraction was used for determination and identification.

Blaser's abbreviated notation[5] was employed for the oxo-anions of phosphorus in the present paper: $PH_2O_2^-$ ($\overset{1}{P}$), PHO_3^{2-} ($\overset{3}{P}$), PO_4^{3-} ($\overset{5}{P}$), $H_2PO_2^-$ ($\overset{2}{P}-\overset{2}{P}$), $P_2HO_5^{3-}$ ($\overset{3}{P}-\overset{4}{P}$), $H_2P_2O_6^{2-}$ ($\overset{4}{P}-\overset{4}{P}$) and $P_2H_2O_5^{2-}$ ($\overset{3}{P}-O-\overset{3}{P}$).

Three different methods for the colorimetric determination of each oxo-anion of phosphorus were carried out by using molybdenum (V)–molybdenum (VI) reagent[6], as follows.

Method A: This is useful for the determination of orthophosphoric acid ($\overset{5}{P}$). A 1-ml volume of molybdenum (V)–molybdenum (VI) reagent is added to 2 ml of each fraction in a test-tube and heated at 100°C for 1 h in a water-bath. After cooling and adjusting the volume of the solution to 20 ml with water, the absorbance is measured.

Method B: This is useful for the determination of total phosphorus, including lower oxo-anions. A 1-ml volume of molybdenum (V)–molybdenum (VI) reagent and 0.5 ml of 1 M sodium hydrogen sulphite are added to 2 ml of each fraction in a test-tube. Other procedures are as in method A. Elution diagrams were usually drawn for the results measured by this method.

Method C: This is useful for the determination of hypophosphoric acid ($\overset{4}{P}-\overset{4}{P}$). A 1-ml volume of molybdenum (V)–molybdenum (VI) reagent is added to 2 ml of each fraction in a test-tube. After adjusting the volume of the solution to 20 ml with water, the absorbance is measured.

The absorbance was measured with a Hitachi 101 spectrophotometer, at 830 nm for orthophosphoric heteropoly blue (for methods A and B) and at 630 nm for hypophosphoric heteropoly blue (for the method C). The detailed procedure for the quantitative determination and the technique of anion-exchange chromatography are similar to those described by Tominaga *et al.*[7].

RESULTS AND DISCUSSION

Fig. 1 shows the elution diagram for the hydrolysis products of freshly prepared P_2I_4 in which solution $\overset{2}{P}-\overset{2}{P}$ anions are produced[4]. The elution was started 15 min after the beginning of hydrolysis of P_2I_4. The elution diagram was drawn for the absorption at 830 nm by applying method B. The inset in Fig. 1 represents the elution diagram obtained for the elution started after 53 h after the hydrolysis of P_2I_4. The dotted line was drawn for the absorbance at 830 nm by using method C (This peak is assigned to $\overset{4}{P}-\overset{4}{P}$ and the most coloured position is fraction 113). The component of $\overset{4}{P}-\overset{4}{P}$ anions is found to increase with the progress of the hydrolysis. The solid line was obtained on the basis of calculation by substituting the absorbance at 830 nm for the coloured fraction by using method C from the absorbance obtained by using method B (the most coloured position of this peak is fraction 118). The elution positions for $\overset{1}{P}$, $\overset{3}{P}$ and $\overset{5}{P}$ anions are determined easily.

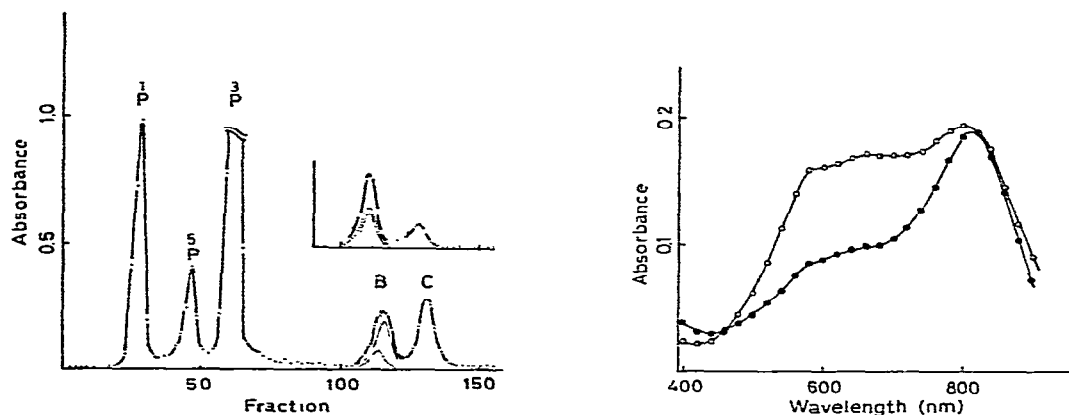Fig. 1. Chromatographic elution curve for the hydrolysed products of P_2I_4. Peaks: B is assigned to a mixture of $\overset{4}{P}-\overset{4}{P}$ and $\overset{2}{P}-\overset{2}{P}$ anions; C is assigned to $\overset{2}{P}-\overset{4}{P}$ anion. Resin: Bio-Rad AG 1-X8 (Cl⁻), 100–200 mesh. Column dimensions: 66 × 1.54 cm I.D. Flow-rate: 1 ml/min. The eluent (pH 6.8) is buffered with 25 ml of 2 M ammonium acetate per litre of eluent. A gradient elution technique was applied by mixing 0.2 M sodium chloride into 750 ml of 0.075 M sodium chloride solution.

Fig. 2. Absorption spectra of (○) fractions 113 ($\overset{4}{P}-\overset{4}{P}$) and (●) 118 (P) in Fig. 1.

Fig. 2 represents the absorption spectra of fractions 113 (peak B1) and 118 (peak B2). The spectrum of fraction 113 shows the overlapped absorption spectrum of orthophosphoric and hypophosphoric heteropoly blue and that of fraction 118 shows the absorption spectrum of orthophosphoric heteropoly blue. Peak B consists of the overlap of peak B1 assigned to $\overset{4}{P}-\overset{4}{P}$ anions and B2 to $\overset{2}{P}-\overset{2}{P}$ anions. The last peak in Fig. 1 is assigned to $\overset{2}{P}-\overset{4}{P}$.

Fig. 3 represents the chromatographic elution diagram for the solution in which the irradiated sodium hypophosphite was dissolved under the same conditions as described in the experimental section. The presence of $\overset{4}{P}-\overset{4}{P}$ anions in this solution was also confirmed because peak B in Fig. 3 shows a pale blue colour on applying
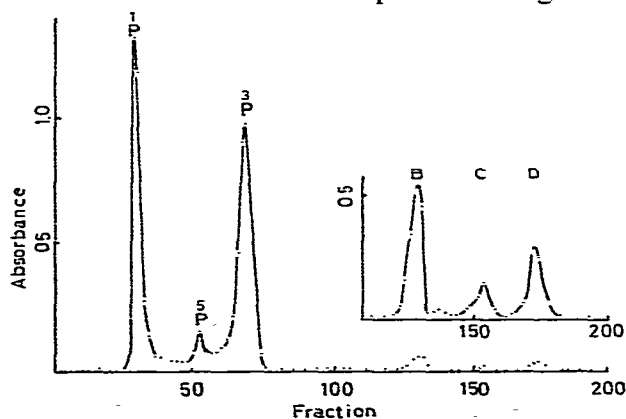

Fig. 3. Chromatographic elution curve for irradiated sodium hypophosphite. Experimental conditions and peaks B and C as in Fig. 1. Peak D is assigned to the $\overset{3}{P}-O-\overset{3}{P}$ anion.

method C. However, the main component of peak B was $\overset{2}{P}-\overset{2}{P}$. Peaks C and D are assigned to be $\overset{2}{P}-\overset{4}{P}$ and $\overset{3}{P}-O-\overset{3}{P}$, respectively, as described later.

The solution in which the irradiated ammonium hypophosphite was dissolved under the conditions described in the experimental section was chromatographed to separate each species. Fig. 4 shows the chromatographic elution curve obtained by using method B. Time t shows the time elapsed between the dissolution of the irradiated ammonium hypophosphite and the onset of the elution of the chromatography. The chemical species are denoted by peaks A, B, C and D as shown in Fig. 4. Peak B of the elution curve for $t = 0$ did not show any colouring, even though method C was applied, but that for $t = 261$ showed a pale blue colour. The chemical species of peaks A, B and D are unstable in acidic solution and their concentrations calculated from Fig. 4 decrease with standing time, as shown in Figs. 4 and 5. Fig. 5 shows that the plots for ln K vs. time (t) are almost linear. K is ratio peak area ($t = t$)/peak area ($t = 0$). If the hydrolysis reactions of the chemical species A, B, C and D are assumed to be first order, the half-life periods of disappearance for peaks A, B, C and D are calculated to be 75, 230, 820 and 40 h respectively, in 10^{-3} M hydrochloric acid at $20°C$.

Peaks C and D are assigned to be $\overset{2}{P}-\overset{4}{P}$ and $\overset{3}{P}-O-\overset{3}{P}$ anions, respectively, because the elution positions C and D are in good agreement with those reported by Tominaga et al.[7]. The $\overset{3}{P}-O-\overset{3}{P}$ anions are known to be comparatively stable in a solution
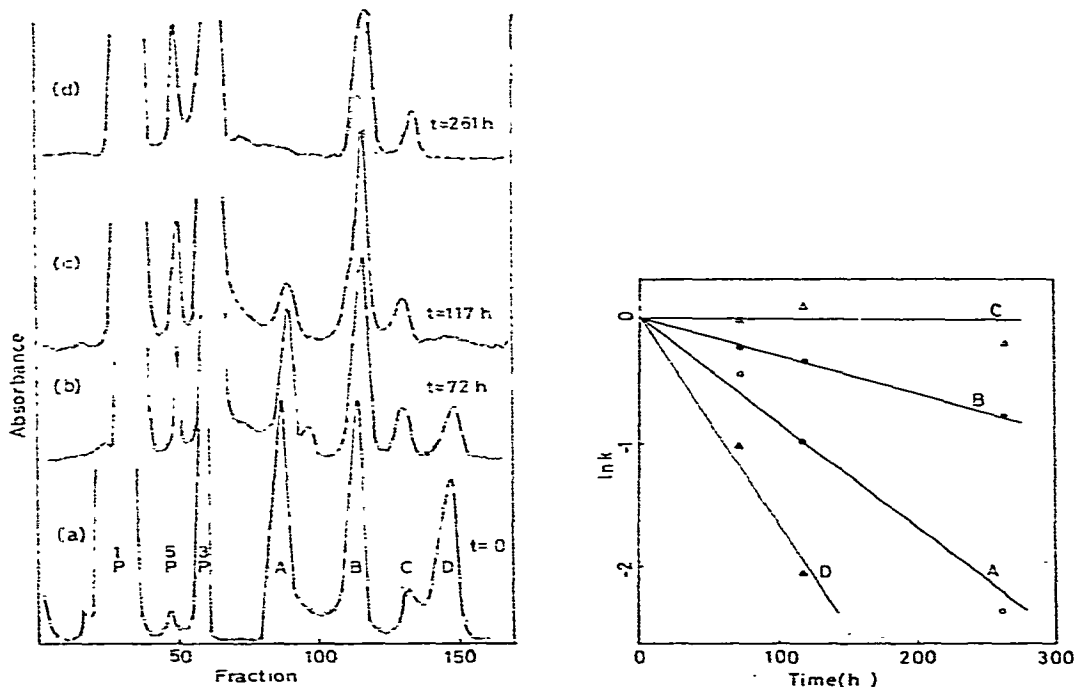

Fig. 4. Variation of the chromatographic elution curves for ammonium hypophosphite with the time elapsed, t, between the dissociation of the sample and the onset of elution. Experimental conditions and peaks as in Fig. 1. Peak A may be assigned to the $\overset{0}{P}-\overset{2}{P}$ anion.

Fig. 5. Plots of K vs. time. K is the ratio peak area ($t = t$)/peak area ($t = 0$). Peak A may be assigned to the $\overset{0}{P}-\overset{2}{P}$ anion. Peaks B, C and D are assigned to $\overset{2}{P}-\overset{2}{P}$ (main species), $\overset{2}{P}-\overset{4}{P}$ and $\overset{3}{P}-O-\overset{3}{P}$ anions, respectively.

of pH range 6–8. The half-life period of the hydrolysis of $\overset{3}{P}-O-\overset{3}{P}$ is reported to be 1000 h at pH 5–7, 60 h at pH 4 at 30°C, and is dependent on the pH of the solution[8]. The difference in the half-life periods of the hydrolysis results in a difference in the pH of the reaction solutions because the solution used here contains a large amount of ammonium hypophosphite (140 mg per 100 ml) in 10^{-3} M hydrochloric acid.

The fractions for elution peak A were collected and dried. The residue was dissolved in concentrated hydrochloric acid, the precipitate of NaCl produced was filtered off and the residue was dried under mild conditions to evaporate hydrochloric acid. The residue was then dissolved in 5 ml of water and introduced on to an anion-exchange column. Its elution diagram indicates the existence of $\overset{1}{P}$ anion (90 %) and $\overset{3}{P}$ anion (10 %). One of the possible chemical species for peak A may be $\overset{0}{P}-\overset{2}{P}$ anions because its anions are hydrolysed to $\overset{1}{P}$ anions in acidic solution. This is analogous to the hydrolysis reaction of $\overset{2}{P}-\overset{4}{P}$ in which $2\overset{3}{P}$ anions are produced. Unfortunately, however, the presence of $\overset{0}{P}-\overset{2}{P}$ has not yet been confirmed. The P–N bonded lower oxophosphorus ions might be eluted more rapidly than their non-amidooxophosphorus ions, because mono-, di- and triamidophosphate ions are eluted in front of the elution position of $\overset{5}{P}$ anions[9]. Therefore, it is doubtful whether peak A should be assigned to be P–N bonded lower oxophosphorus. However, this peak appears only on the elution curve of irradiated $NH_4H_2PO_2$, which suggests that the chemical species of peak A may have a P–N bond.

The elution positions of peak B in Figs. 1, 3 and 4 are consistent with each other. The $\overset{4}{P}-\overset{4}{P}$ anions are eluted down the column in front of $\overset{2}{P}-\overset{2}{P}$ anions, and so it is expected that $\overset{2}{P}-\overset{2}{P}$ anions will show stronger bonding with anion exchangers.

Morton[10] recognized a radical $O_2P-PHO_2^{2-}$ in γ-irradiated $NH_4H_2PO_2$ crystals on the basis of ESR spectra. This radical ion can produce $\overset{2}{P}-\overset{2}{P}$ anions in the hydrolysis of the irradiated samples. Disproportionation reactions may take place in the solid because the formation of phosphine and yellow phosphorus is observed during the hydrolysis of the irradiated samples in acidic solution.

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