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Formation of Hypophosphate in the Radiolysis of Phosphite Solution

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The formation of hypophosphate and phosphate in the radiolysis of a phosphite solution was established by the anion-exchange chromatographic technique. The quantitative determination of their yields was made by colorimetry of the phosphate and hypophosphate with the Mo(V)+Mo(VI) reagent, which develops molybdenum-blue colors in two steps at different temperatures. The G values in an aerated condition are 0.01 molecules/100 eV in acid and 0.1 molecule/100 eV in neutral pH with respect to the hypophosphate formation, independent of the phosphite concentration. In a deaerated system much higher values are obtained, amounting to around 0.5 molecules/100 eV at a phosphite concentration of 10^{-3} M. The G values of hypophosphate plus phosphate are around 3.0; this is in agreement with the half-value of the primary radical yields, $1/2\cdot(g_{\mathrm{red}}+g_{\mathrm{OH}})$, reported in the data derived from the radiation-chemical studies in the aqueous system. The hypothesis that the hypophosphate (IV) ion radical is a transient species in the oxidation of phosphite to phosphate is supported by the results obtained in this work.

The neutron activation of phosphate in an aqueous solution produces ^{32}P-labelled hypophosphate simultaneously with other oxyphosphorus compounds of different oxidation numbers.1) However, we failed in an attempt to prepare hypophosphate from phosphite by oxidation in an aqueous medium, despite its high stability and inertness.2) The synthesis of labelled hypophosphate could not be ascribed absolutely to the recoil process of ^{32}P hot atoms, because the transformation of a primary product of labelled phosphite into hypophosphate under ambient radiations in nuclear reactor might be involved. Cottin and Haissinsky3) proposed a reaction mechanism for the radiolysis of phosphite to phosphate in the aqueous phase by assuming that the hypophosphate-ion radical is a transient intermediate. Hypophosphate-ion radicals have been detected by ESR study in a gamma-irradiated orthophosphate in the form of $\cdot H_2PO_3$.4) The

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1) N. Matsuura and Tsing-Ko Lin, *J. Inorg. Nucl. Chem.*, **32**, 353 (1970).

2) A. D. Mitchell, *J. Chem. Soc.*, **125**, 1013 (1924); Van Wazer, "Phosphorus and Its Compounds," Vol. I, Interscience Pub., New York (1958), pp. 406—411.

3) M. Cottin and M. Haissinsky, *J. Chim. Phys.*, **53**, 917 (1951).

4) A. Treinin, "Radical Ions," Interscience Pub., New York (1968), p. 525.

defect formed by gamma-irradiation in glassy P_2O_5 or glassy alkaline phosphate has been ascribed to this radical,[5] but with no chemical evidence. Haissinsky's report stated that the hypophosphate-ion radicals produced during the radiolysis of phosphite were oxidized further by certain additives, such as O_2, H_2O_2, and N_2O, and that there was little chance to form hypophosphate by a recombination of $\cdot H_2PO_3$.[6] A new technique of the colorimetry of hypophosphate developed by Ohashi *et al.*[7] is now available for determining the yields of hypophosphate in the radiolysis of phosphite by the application of the Mo(V)+Mo(VI) reagent.[8]

Experimental

Materials and Reagents. Sodium phosphite salt, $Na_2HPO_3\cdot 5H_2O$, was purchased from Wako Pure Chemicals Co., Ltd., and was used without purification. Sodium hypophosphate salt was prepared from elemental phosphorus by hypochlorite oxidation according to the procedure described in the literature.[9] Triply-distilled water was used for preparing the samples to be irradiated.

Irradiation. The sample solutions, in Pyrex tubes, were irradiated with ^{60}Co gamma-ray source (3.8×10^{18} eV/g·hr at 10 cm from the center); the experiments were done in the Institute for Solid State Physics, The University of Tokyo. Irradiations were performed at room temperature, and the absorbed gamma-dose was calibrated by means of a Fricke dosimeter under the same conditions as were used for the irradiation of the samples by assuming $G(+Fe^{3+})=15.5$.

Chemical Analysis. For the detection of hypophosphate the development of the molybdenum-blue color by Mo(V)+Mo(VI) reagent[8] was effected in three different stages. First, a sample solution kept for 30 min at 25°C after the addition of the reagent develops a full color as a result of the hypophosphate. Second, heating on a boiling water bath for some ten minutes results in an increase in the blue color by an amount corresponding to the orthophosphate concentration. Finally, the color due to phosphite is developed on a separate sample solution by the use of the same reagent, with acid sulfite added. The last treatment provides the total content of the oxyphosphorus acid present in the irradiated solution. A batch test tried on synthetic samples showed a slight deviation in the observed values from the expected values as a result of background absorption by the successive treatment of the color development. On the basis of the batch-test data, a correction was made on the measured absorbancies, but it amounts to less than 10%, depending on the amounts of phosphate and hypophosphate present. A phosphite solution, when heated at near the boiling point of water, degrades into phosphate and hydrogen or phosphine.[10] If phosphite is concentrated too much in a sample solution, the "autoredox" decomposition of phosphite also affects the results of the absorbancy by augmenting the phosphate content during the heat treatment for the color development in the second stage. However, the background absorbancy caused by the thermal degradation of phosphite can be disregarded if the phosphite concentration is less than 10^{-3} M. According to our observations, the rate of phosphate formation was proportional to the square of the phosphite concentration, but independent of the concentration of dissolved oxygen. A sharp increase in phosphate was observed at a phosphite concentration higher than about 10^{-3} M. For this reason, the measurements of the radiation-induced yields of phosphate from phosphite were carried out at the concentrations lower than 10^{-3} M.

The ion-exchange chromatographic separation of hypophosphate from phosphate and phosphite was effected by the gradient elution technique, running 0.1 to 0.3 M KCl solutions through a 20-cm Dowex 1×8 anion-exchange resin column. Each 5-m*l* fraction was subjected to colorimetry by the molybdenum-blue method.

Results and Discussion

Evidence for the formation of hypophosphate in an irradiated solution of phosphite was given by the chromatographic technique combined with the colorimetry of phosphorus by the molybdenum-blue method. Gradient elution with 0.1 M to 0.3 M potassium chloride solutions, buffered with borate at pH 8 develops the phosphoxy-acids of different oxidation states in the order of: hypophosphite, phosphate, phosphite, and hypophosphate. The elution peak at 190 m*l* in the chromatographic pattern shown in Fig. 1 can be assigned to the peak due to hypophosphate.[11] The yield of hypophosphate in the radiolysis of the phosphite solution was computed from the area of the chromoatogram peak, whose value was in good agreement with the value found by the differential colorimetry of hypophosphate.

A systematic survey of the yields of hypophosphate in the radiolysis of phosphite was made by the differential-colorimetric method both in 0.5 N sulfuric acid and in a neutral solvent under aerated or deaerated conditions. The yields are plotted against the absorbed gamma-dose for a given concentration

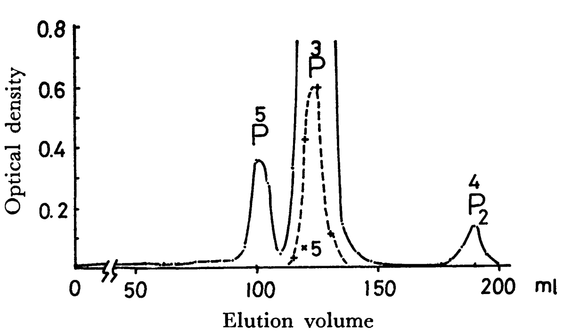

Fig. 1. Chromatographic analysis of gamma-irradiated phosphite solution.
2 m*l* of 5×10^{-3} M phosphite solution was adsorbed on the anion-exchange resin Dowex 1-8, subjected to gradient elution with 0.1 to 0.3 M KCl and each 5 m*l* fraction was under examination for phosphorus content by Mo(V)+Mo(VI) reagent

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[5] T. Feldmann and N. Treinin, *J. Chem. Phys.*, **47**, 2754 (1967); *J. Phys. Chem.*, **72**, 3768 (1968).

[6] M. Haissinsky, *J. Chim. Phys.*, **62**, 1141, 1149 (1965).

[7] N. Yoza and S. Ohashi, This Bulletin, **37**, 33, 37 (1964).

[8] F. Lucena-Conde and L. Prat, *Anal. Chim. Acta*, **16**, 473 (1957).

[9] E. Leininger and T. Chulski, "Inorganic Synthesis," Vol. IV, ed. by J. C. Bailar, McGraw Hill, New York (1953), p. 68.

[10] Van Wazer, *loc. cit.*, p. 380.

[11] N. Matsuura, M. Kobayashi, and Tsing-Ko Lin, This Bulletin, **43**, 2850 (1970).

of phosphite in Fig. 2. These plots provide a straight line falling on the abscissa at a point corresponding to the gamma-dose of around 2×10^{17} eV/m*l* for the radiolysis in both acid and neutral media, irrespective of the presence of oxygen. In an acid medium under aerated conditions, there is practically no formation of hypophosphate, as may be seen in Fig. 2.

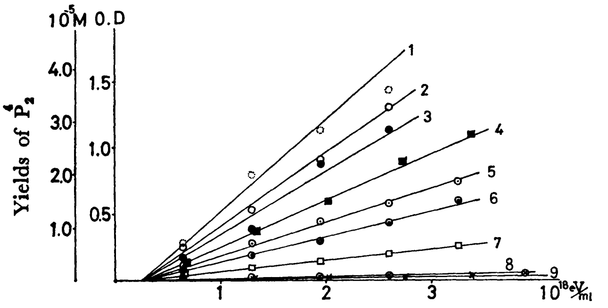
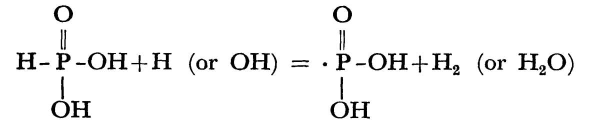


Fig. 2. Yields of hypophosphate ($\overset{4}{P}_2$)-gamma dose relationship.

1. (○) phosphite concentration of 10^{-3} M
2. (○) 5×10^{-4} M
3. (●) 10^{-4} M in neutral pH
4. (■) 10^{-3} M
5. (⊙) 5×10^{-4} M
6. (◎) 10^{-4} M in acid under deaerated condition
7. (□) 5×10^{-4} M in neutral pH
8. (⊗) 5×10^{-4} M
9. (×) 10^{-4} M in acid under aerated condition

The radiation-chemical yields in *G* value were determined at a gamma-dose of 6.4×10^{17} eV/m*l* as a function of the phosphite concentration. The results are represented in Fig. 3. The *G* value of hypophosphate formation in an aerated neutral solution attains a value of 0.1 ions per 100 eV, independent of phosphite concentration. In a deaerated solution, on the other hand, the *G* values increase with an increase in the concentration of phosphite. The hypophosphate detected in the radiation-induced oxidation of phosphite to phosphate is strong evidence that the hypophosphate-ion radicals are in the monomer form, produced as transient intermediates and acting as precursors of hypophosphate. The fact that the yields of hypophosphate are greatly influenced by the concentration of phosphite is connected with the properties of the hypophosphate-ion radicals, which are relatively inert to the radical species of water radiolysis as compared with the reactivity of the phosphite. The reaction between the phosphite and hydrogen peroxide occurs only very slowly, while it proceeds at an appreciable rate under the influence of ultra-violet rays, which generate the OH radicals by the decomposition of hydrogen peroxide. The hypophosphate is described in the literature as being resistant to the attack of the common redox reagents. In our experiments, too, the yields of phosphate from hypophosphate in the radiolysis were observed to be relatively small and to be entirely suppressed in the presence of phosphite.

From these facts and observations, we assumed that the radiolysis of phosphite was initiated through process (1) by the abstraction of the hydrogen atom from the P–H bond of phosphite ions:



$$\text{H-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}\text{-OH} + \text{H (or OH)} = \cdot\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}\text{-OH} + \text{H}_2 \text{ (or H}_2\text{O)} \qquad (1)$$

The hypophosphate radicals thus formed are oxidized further into phosphate by the OH radicals, but the rate of oxidation may be slowed down so long as phosphite is predominant as a powerful radical scavenger. When the hypophosphate-ion radicals are accumulated to a certain extent by the absorption of the critical gamma-dose, the recombination reaction through (2) competes with the oxidation by the OH radicals through (3):

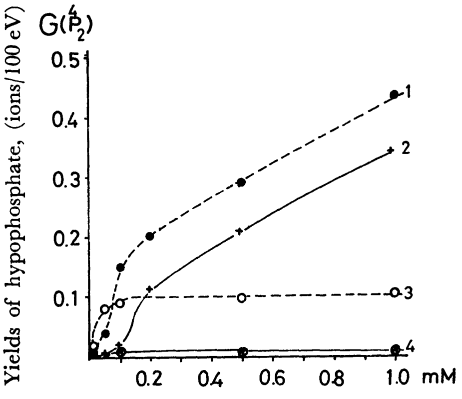


Fig. 3. *G* values of hypophosphate formation as fnuction of phosphite concentration.
1. in deaerated neutral solution, 2. deaerated acid solution, 3. aerated neutral solution, and 4. aerated acid solution

$$2\cdot H_2PO_3 = H_4P_2O_6 \qquad (2)$$

$$\cdot H_2PO_3 + OH = H_2PO_4^- + H^+ \qquad (3)$$

Since, $G(H_2)=g_{H_2}+g_H$ has been known in the acid radiolysis of phosphite,[3] the reduction of the hypophosphate radical to phosphite by the reducing radicals to provide $G(H_2)=g_{H_2}+g_H/2$ is improbable. However, in the presence of oxygen, the H atoms acting as reducing agents are converted into the HO_2 radicals through (4) as the oxidizing agent, and the reducing radicals in turn take part in the oxidation of the hypophosphate radicals through (5):

$$H + O_2 = HO_2 \qquad (4)$$

$$\cdot H_2PO_3 + HO_2 + H_2O = H_3PO_4 + H_2O_2 \qquad (5)$$

Consequently, the low yields of hypophosphate in the radiolysis under aerated conditions can be explained by the contribution of the HO_2 radical to phosphate formation by reactions (4) and (5) in stead of to hypophosphate formation in the dimer form by (2).

The yields of phosphate in the radiolysis of phosphite were determined by differential colorimetry, along with the yields of hypophosphate. The *G* values of phosphate formation plus hypophosphate formation, thus determined, are shown in Fig. 4 as a function of the phosphate concentration. The results show that the *G* values tend to attain a certain limiting value at a concentration of phosphite higher than 10^{-4} M beyond this concentration all the radical products of water

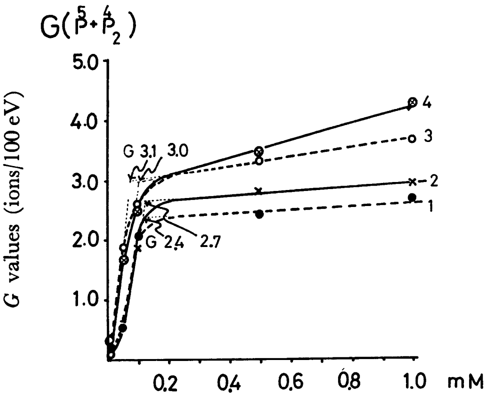


Fig. 4. G values of phosphate plus hypophosphate as function of phosphite concentration in
1. deaerated neutral solution, 2. deaerated acid solution, 3. aerated neutral solution, 4. aerated acid solution.

radiolysis that escape from recombination in the spur space are swept away by the phosphite. The steep rises in the curves, followed by plateaus, make it possible to find the lowest concentration of phosphite necessary for fulfilling the above-cited conditions by the extension of the ascending and plateau parts of the curve, as is shown in Fig. 4. At these particular points, the G values are from 2.4 to 2.7 for the radiolysis in the deaerated system and from 3.0 to 3.1 for the radiolysis in the aerated system.

Since the conversion of phosphite to phosphate is a two-equivalent oxidation, these G values must be a half of the sum of the primary radical yields with respect to the OH and the reducing species. Accordingly, the G values of phosphate plus hypophosphate shown in Fig. 4 can be interpreted in terms of the primary radical yields, denoted by g_{OH} and g_H as below by (6). According to (6), the observed value of G agrees well with the theoretically-derived value,[12] 3.35 at pH 0.2 or 3.5 at pH 6.0:

$$G(\overset{5}{P} + \overset{4}{P}_2) = 1/2 \cdot (g_H + g_{OH}) \qquad (6)$$

In (6) g_H implies the primary yields of the reducing radicals, the H atoms as well as the solvated electrons.

In our experiment, the G values steadily increase beyond 10^{-4} M of phosphite, and at 10^{-3} M the observed G value is 4.3 in the aerated-acid medium. However, an extraordinary G value by the chain mechanism has not yet been observed. The slow increase, followed by a rapid rise in $G(\overset{4}{P}_2+\overset{5}{P})$, can be ascribed to the fact that radical products remaining alive in the spurs come to be partially scavenged by phosphite. The contribution of hydrogen peroxide from the molecular product of radiolysis to the increasing $G(\overset{4}{P}_2+\overset{5}{P})$ can not be excluded, particularly in the aerated system, even though the rate of the reaction of hydrogen peroxide with phosphite is very slow where there is no influence of radiation. Since there is no formation of hypophosphate below a critical gamma-dose of about 2×10^{17} eV/ml, denoted by D_{crit}, the hypophosphate ion radicals must attain a stationary concentration amounting to $2G\cdot(\overset{4}{P}_2+\overset{5}{P})\cdot D_{crit}$. The stationary concentration of the hypophosphate ion radicals under consideration is around 2×10^{-5} M, if the $G(\overset{4}{P}_2+\overset{5}{P})$ value is taken to be 3.0 on the average. The latter concentration is about ten times smaller than the phosphite concentration, giving plateau G values, 1×10^{-4} M. By comparing the phosphite concentration of 10^{-4} M for reaction (1) with the hypophosphate ion radical concentration of 2×10^{-5} M for reaction (2), a majority of the radical OH can be said to react with phosphite through (1) unless the second-order rate constant of (1) is much smaller than that of (3). Our results show that the phosphate formation (3), which is at least ten times larger than that of reaction (1).

In connection with the protective action of phosphite, the effect of hypophosphite was studied in order better to understand the critical dose, D_{crit}, in this system. If hypophosphite solution is irradiated with gamma-rays, no phosphate is formed and the increase of phosphite continues until a greater part of the hypophosphite is consumed. Thus, the oxidation of phosphite to phosphate is entirely protected against the attack of the radical products of water radiolysis, as may be seen in Fig. 5. The critical gamma-dose for the complete protection of phosphate formation was 1.0×10^{18} eV/ml. At this critical value, the hypophosphite concentration is lowered significantly to such an extent that the rate of oxidation of phosphite to phosphate becomes compatible with the rate of the conversion of hypophosphite to phosphite.

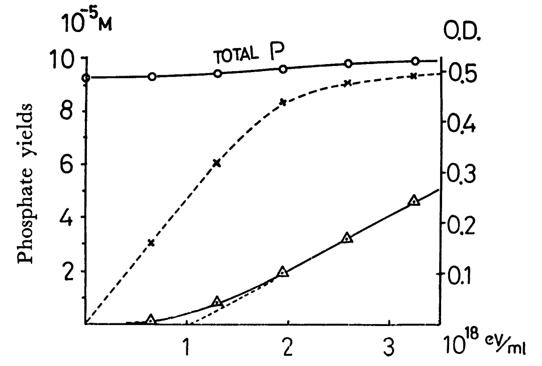


Fig. 5. Yields of phosphate ($\overset{5}{P}$) in the radiolysis of 10^{-4} M hypophosphite (full line curve with △).
Total phosphorus content, including hypophosphite, phosphite, hypophosphate, and phosphate, for checking the amount lost by thermal degradation during the heat treatment of color development (upper full line with ○).
For the sake of comparison the yields of phosphate in the radiolysis of the same concentration of phosphite solution are plotted by the break line with ×.

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[12] E. Hayon, "Radiation Chemistry of Aqueous Systems," ed. by G. Stein, Interscience Pub., Jerusalem (1968).