The Radiation Annealing of Phosphorus-32 with Cobalt-60 Gamma-rays for Several Neutron-irradiated Inorganic Phosphorus Compounds

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The distribution of chemical species formed by neutron capture in several oxy-acids has been shown to depend on thermal and radiation effects during neutron irradiation in a nuclear reactor.

Boyd, Cobble and Wexler[1] pointed out that the chemical yield of bromine-82 as bromide was considerably influenced by the time of neutron irradiation in a reactor when the bromine-82 of a high specific activity was produced by the Szilard-Chalmers effect in potassium bromate. They showed that the shorter the irradiation time in a reactor, the higher the chemical yield of bromine-82 of a high specific activity. Cobble and Boyd[2] also indicated that the retention as bromate was increased by re-irradiation with cobalt-60 gamma-rays for neutron-irradiated potassium bromate. Maddock and Müller[3] observed that the retention increased in neutron-irradiated calcium bromate when it was re-irradiated with 1.8 MeV. electrons. Green, Harbottle and Maddock[4] noticed that the distribution of chemical species containing chromium-51 formed by the neutron irradiation of potassium chromate in a reactor was changed by re-irradiation with gamma-rays. Claridge and Maddock[5] reported that the retention increased for potassium dihydrogen phosphate and ammonium

1) G. E. Boyd, J. W. Cobble and S. Wexler, *J. Am. Chem. Soc.*, **74**, 237 (1952).
2) J. W. Cobble and G. E. Boyd, ibid., **74**, 1282 (1952).
3) A. G. Maddock and H. Müller, *Thans. Faraday Soc.*, **56**, 509 (1960).
4) J. H. Green, G. Harbottle and A. G. Maddock, ibid., **49**, 1413 (1953).
5) R. F. C. Claridge and A. G. Maddock, "Chemical Effects of the Nuclear Transformations," Vol I, IAEM, Prague (1961), p. 475.

hydrogen phosphate when they were irradiated with 1.8 MeV. electrons or an ultraviolet light. However, their results are somewhat ambiguous, as has been pointed out by Wazer,[6] because they used the precipitation method in separating the chemical species.

In their recent paper, Baba, Tanaka and Yoshihara[7] reported that the retention increased in several neutron-irradiated phosphates when they were thermally treated; in their experiment, the chemical species were separated by one-dimensional paper-partition chromatography. They observed that all phosphorus-32 species other than parent species decreased when heated for over 10^4 min. in the temperature range of 85～200°C. The rate of the decrease in the polyphosphate was larger than that of the reduced species. The fractional amount of the reduced species was extremely small[8] at long irradiations or at irradiations at a high power operation in nuclear reactors. This fact can not be explained by the process expected from the thermal annealing experiments. In the preparation of phosphorus-32 of a high specific activity by the Szilard-Chalmers effect,[9] the decrease in the recovery might be attributed to the radiation annealing effect. In the present paper, radiation annealing with cobalt-60 gamma-rays was studied for several neutron-irradiated inorganic phosphorus compounds, mainly in dehydrated forms.

Experimental

Target Materials.—Series of sodium orthophosphates and potassium orthophosphates, sodium orthophosphates, sodium orthophosphite, sodium hypophosphite and sodium pyrophosphate were used in anhydrous forms. Hydrated salts were dehydrated by heating and then drying them in vacuo over phosphorus pentoxide overnight. The anhydrous salts thus prepared were assayed for purity by the radioactivation method and by flame photometry, as has been previously reported[7].

Neutron Irradiation.—The salts were sealed in a polyethylene tube and subjected to neutron irradiation in hole No. 12 (a vertical hole; the nominal neutron flux was 0.48×10^{12} n/cm^2-sec.) for 15 hr. and in hole No. 16 (a pneumatic tube, the nominal neutron flux was 0.64×10^{12} n/cm^2-sec.) for 2 hr. in JRR-1 (a waterboiler type, operated at 40 kW.). Immediately after irradiation, the samples were cooled with dry ice to avoid any change in the distribution of the chemical species containing phosphorus-32 during storage.

Gamma-ray Irradiation.—Neutron-irradiated samples were again sealed in a polyethylene tube or in a glass ampoule and exposed to high intensity gamma-rays from a cobalt-60 source of 0.7×10^4 curies in a thermally-controlled vessel at temperatures from −196°C to 100°C. The irradiated samples were then stored in a vessel cooled with dry ice.

Chemical Separation.—The chemical species containing phosphorus-32 were separated by one-dimensional paper-partition chromatography by the same procedure as before.[7] The decomposition of the sample by gamma irradiation was measured by colorimetric analysis of the products separated from the parent species by the anion exchange method.[10,11]

Counting Procedure.—After it had been developed and dried, the paper was cut into pieces 1 cm. wide and the radioactivity was measured by a thin end-window-type GM counter at a constant geometry. Counting was made at least ten days after the termination of neutron irradiation in order to avoid errors from the radioactivity of sodium-24 or potassium-42.

Thermal Annealing.—Neutron-irradiated sodium orthophosphates were subjected to thermal annealing at an elevated temperature, as has been previously reported,[7] and the effect of neutron irradiation conditions on thermal annealing behaviors was tested for the phosphorus-32 species. The distribution of chemical species containing phosphorus-32 obtained from irradiation for 2 hr. in a pneumatic tube was considerably different from that of 15 hr. irradiation in the vertical hole of the JRR-1. In both cases, however, all the chemical species other than parent species decreased, only the parent species increased with the salts were heated, and the polyphosphate was more predominantly annealed than the reduced species. It was concluded that the thermal-annealing behavior does not depend on the neutron irradiation conditions. All samples were stored in two vessels: one portion was stored at 30°C, and the other at a lower temperature obtained by cooling with dry ice. During the storage for 16 days, no change was observed in the distribution of chemical species containing phosphorus-32.

Results and Discussion

The Decomposition of the samples by Gamma-ray Irradiation.—When the phosphate salts are irradiated by gamma-rays, the decomposition of the sample may be expected as a result of radiation effects. Pyrophosphate was detected in the gamma-irradiated orthophosphates. Except for the case of dipotassium hydrogen phosphate, the amounts of pyrophosphate formed by gamma irradiation were so small that the amounts detected were near the detection limit (approximately 5 μg. per gram of the sample),

6) J. R. Van Wazer, "Phosphorus and its Compounds," Vol. I, Interscience Publishers, Inc., New York (1957), p. 441.

7) H. Baba K. Yoshihara, H. Amano, K. Tanaka and N. Shibata, This Bulletin, **34**, 590 (1961); H. Baba, K. Tanaka and K. Yoshihara, ibid., **36**, 928 (1963).

8) K. Tanaka, to be published.

9) K. Tanaka, to be published.

10) H. J. Weiser, Jr., *J. Am. Oil Chemists' Soc.*, **34**, 124 (1957).

11) N. Shibata K. Yoshihara, K. Tanaka, H. Baba and K. Kurosawa, Fifth Conference of Radioisotopes in Japan, B/P-C 10 (1963).

TABLE I. ESTIMATED G VALUES FOR PYROPHOSPHATE FORMATION OF SEVERAL ORTHOPHOSPHATES

Target material	G Values	
	20°C	50°C
NaH_2PO_4	0.17	−0.16
Na_2HPO_4	0.11	0.15
Na_3PO_4	0.075	0.08
KH_2PO_4	0.05	0.02
K_2HPO_4	<1.4	<1.5

even at the total dose of 1×10^7 r. The estimated G values of pyrophosphate formation are tabulated in Table I. Pyrophosphate was also formed when orthophosphates containing hydrogen in the molecule were heated above 150°C. Because pyrophosphate formation in the orthophosphate salts was prominent as a result of thermal reaction at an elevated temperature, the effects of gamma-rays on the formation of pyrophosphate could not be detected in this case. The formation curves obtained by irradiation at temperatures of 150∼200°C for sodium dihydrogen phosphate and disodium hydrogen phosphate were exactly the same as those obtained by the thermal reaction, within the range of experimental error. The formation of no polyphosphates other than pyrophosphate was observed by the anion exchange separation for all samples. The evolution of gaseous products was not studied; this evolution may be disregarded considering the results obtained by Sellers and his co-workers.[12]

The Change by Gamma Irradiation of the Chemical Species Containing Phosphorus-32.— The distribution of chemical species containing phosphorus-32 in neutron-irradiated phosphates varies with the irradiation conditions in the reactor. All the salts were irradiated in the same capsule to compare the annealing effects of irradiation for the different salts.

The radiation annealing of species containing phosphorus-32 in several orthophosphate salts (irradiated for 2 hr., in a pneumatic tube of the JRR-1 and re-irradiated with cobalt-60 gamma-rays at −50°C) results in an increase in retention and in a decrease in the reduced species. The behavior of the polyphosphates in irradiation varies considerably among the different orthophosphates studied. The results are shown in Figs. 1—3, where the fraction of each species is plotted against the radiation dose. The retention as orthophosphate increases rapidly in the low dose region and gradually in the higher dose region. This is more prominent in the case of sodium dihydrogen phosphate. The polyphosphate in di-

12) P. A. Sellers, T. R. Sato and H. H. Strain, *J. Inorg. Nucl. Chem.*, 5, 31 (1957).

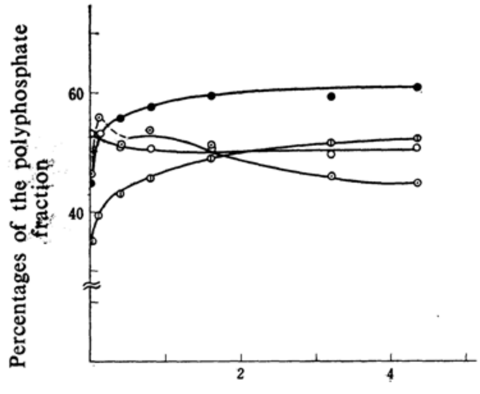

Fig. 1. Gamma ray annealing of ^{32}P in the polyphosphate fraction.

—○— NaH_2PO_4 —●— Na_2HPO_4
—⦶— Na_3PO_4 —⊙— KH_2PO_4

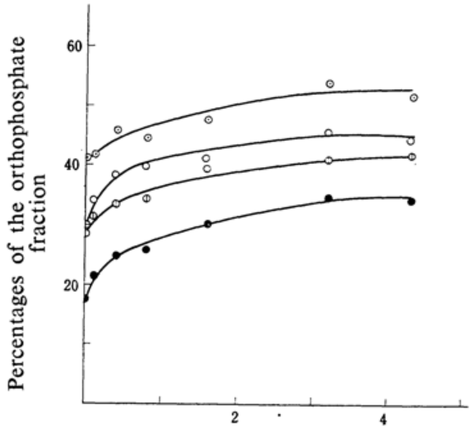

Fig. 2. Gamma ray annealing of ^{32}P in the orthophosphate fraction.

—○— NaH_2PO_4 —●— Na_2HPO_4
—⦶— Na_3PO_4 —⊙— KH_2PO_4

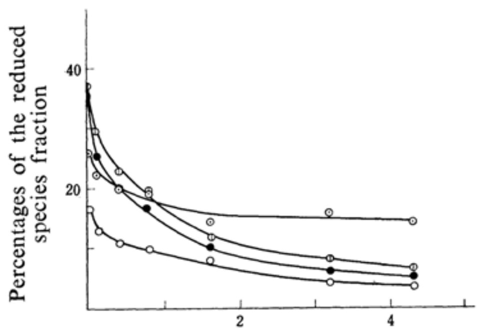

Fig. 3. Gamma ray annealing of ^{32}P in the reduced species fraction.

—○— NaH_2PO_4 —●— Na_2HPO_4
—⦶— Na_3PO_4 —⊙— KH_2PO_4

sodium hydrogen phosphate and in trisodium phosphate shows a fast rise in the initial low-dose region and gradually approaches a plateau, whereas the polyphosphate in sodium dihydrogen phosphate initially increases and then decreases. However, the reduced species clearly decreases in all of the orthophosphate salts studied. These changes in fractions are summarized in Fig. 4 for disodium hydrogen phos-

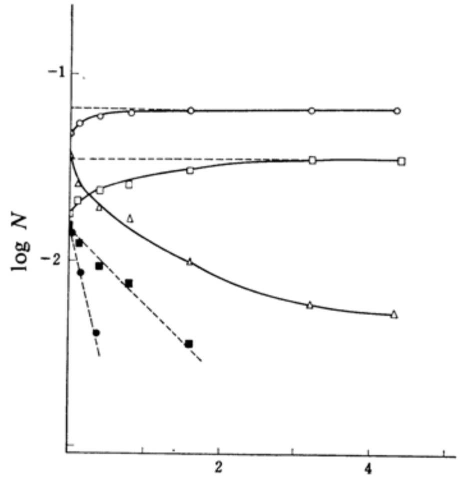

Fig. 4. Gamma ray annealing of the chemical species containing ^{32}P in disodium hydrogen phosphate.

—○— the polyphosphate fraction
—□— the orthophosphate fraction
—△— the reduced species fraction
--■-- estimated increase of the orthophosphate fraction
--●-- estimated increase of the polyphosphate fraction

phate. In the figure, experimental results are given by the solid line, while the dotted lines show the estimated values obtained by the analysis of the curves, assuming the plateau values for each corresponding curve.

The estimated values for the increase in the polyphosphates and those for the orthophosphate are linear on a semilog plot. This suggests that the reactions in the increase in the polyphosphates and orthophosphate follow the first order kinetics, in which the sum of these increases in two fractions corresponds to the decrease in the reduced species. The number of species in the sample is proportional to their percentages in the sample. The ordinates show the logarithmic number of species on an arbitrary scale. By an analysis of these curves, two main processes of the radiation annealing of species containing phosphorus-32 are indicated: (I) the reduced species to the polyphosphate, and (II) the reduced species to the orthophosphate. The reduced species is converted to the phosphorus(V) state by oxidation with a potassium permanganate solution, whereas the polyphosphate is not changed. The polyphosphate is converted to the orthophosphate by hydrolysis with a mineral acid such as hydrochloric or sulfuric acid. The polyphosphate thus contains phosphorus(V). The radiation-induced oxidation process is a predominant reaction in the radiation annealing of orthophosphate salts. This finding is in good agreement with the recent results of Claridge and Maddock[13] which have indicated that phosphorus(III) is oxidized to phosphorus(V) by irradiation with an ultraviolet light or by 1.8 MeV. electrons in several neutron-irradiated phosphates.

The radiation-annealing curves obtained by 15 hr. irradiation in a reactor (with a vertical hole of the JRR-1) seemed to be similar to those by shorter irradiations, except that the polyphosphate fraction is slightly lower in the former. Besides the two main processes stated, other processes were observed; the third process III, the polyphosphate to the orthophosphate, is indicated by the results listed in Table II. The decrease in the polyphosphate at longer irradiations in a reactor suggests that the polyphosphate curve. in Fig. 4 shows a pseudoplateau attained by the rate equilibrium between the two processes, " the reduced species to the polyphosphate " and " the polyphosphate to the orthophosphate." The polyphosphate fractions in the other orthophosphate salts studied show the same behavior as that in disodium hydrogen phosphate.

Annealing behaviors were also studied for neutron-irradiated sodium orthophosphite and sodium hypophosphite. Little change was observed in the distribution of chemical species containing phosphorus-32 in gamma irradiation in the dose range from 1.0×10^6 to 1.5×10^7 r. for these two salts. The hypophosphite fraction in sodium orthophosphite and the orthophosphite fraction in sodium hypophosphite salts were found to be unchanged.

The Effect of the Dose Rate.—The dose-rate dependence of the annealing behavior was studied in the dose range of 3.7×10^4 to 2.1×10^6 r./hr. at the total dose and at the temperature used above. The results obtained are shown in Table II. Only slight differences are observed among the different dose rates.

The Rate Constants in Gamma-ray Annealing.—Assuming that the radiation annealing of chemical species containing phosphorus-32

13) R. F. C. Claridge and A. G. Maddock, *Trans. Faraday Soc.*, **59**, 935 (1963).
14) R. R. Williams, *J. Phys. Colloid Chem.*, **52**, 603 (1948).

TABLE II. TYPICAL EXAMPLE OF LONGER IRRADIATION IN A REACTOR AND DOSE RATE DEPENDENCIES OF THE CHEMICAL DISTRIBUTION OF ^{32}P

Target materials	Neutron irradiation in a JRR-1 reactor n/cm² sec.	^{60}Co gamma ray irradiation: Dose rate r./hr.	Total dose r.	Percentages of each fraction of species (^{32}P): Ortho-phosphate	Poly-phosphate	Reduced species
Na_2HPO_4	2 hr. at 5.0×10^{11}	0	0	17.3	45.4	33.8
	2 hr. at 5.0×10^{11}	3.7×10^4	1.5×10^7	22.0	60.4	17.6
	2 hr. at 5.0×10^{11}	1.7×10^5	1.5×10^7	19.1	62.9	18.0
	2 hr. at 5.0×10^{11}	2.1×10^6	1.5×10^7	22.6	56.4	20.9
Na_2HPO_4	15 hr. at 1.9×10^{11}	0	0	40.4	52.5	7.0
	15 hr. at 1.9×10^{11}	1.2×10^5	4.8×10^6	42.7	52.2	5.2
	15 hr. at 1.9×10^{11}	1.2×10^5	1.5×10^7	45.8	49.6	4.8
	15 hr. at 1.9×10^{11}	2.2×10^5	1.5×10^7	45.5	49.8	4.7
	15 hr. at 1.9×10^{11}	4.7×10^5	1.5×10^7	47.3	49.1	3.4
	15 hr. at 1.9×10^{11}	2.2×10^5	5.2×10^7	53.2	43.9	3.3
NaH_2PO_4	2 hr. at 5.0×10^{11}	0	0	31.4	45.3	23.4
	2 hr. at 5.0×10^{11}	3.7×10^4	1.5×10^7	33.9	60.0	6.1
	2 hr. at 5.0×10^{11}	1.7×10^5	1.5×10^7	35.4	60.1	4.5
	2 hr. at 5.0×10^{11}	2.1×10^6	1.5×10^7	37.5	55.9	6.6
KH_2PO_4	2 hr. at 5.0×10^{11}	0	0	36.6	52.9	10.4
	2 hr. at 5.0×10^{11}	3.7×10^4	1.5×10^7	39.1	58.3	2.6
	2 hr. at 5.0×10^{11}	1.7×10^5	1.5×10^7	39.6	58.6	1.7
	2 hr. at 5.0×10^{11}	2.1×10^6	1.5×10^7	38.0	58.7	3.3

TABLE III. RATE CONSTANTS FOR THE CHANGES OF CHEMICAL SPECIES CONTAINING ^{32}P BY GAMMA IRRADIATION

Target material	Rate constants, hr^{-1}, 1.7×10^5 r./hr. Irradiated at −50°C: k_1*	k_2**	Irradiated at 20°C: k_1	k_2	k_3***
NaH_2PO_4	uncertain	9×10^{-2}	1×10^0	3×10^{-1}	1.8×10^{-3}
Na_2HPO_4	4.7×10^{-2}	2.5×10^{-2}	6×10^{-1}	4.5×10^{-2}	1.5×10^{-3}
Na_3PO_4	2.7×10^{-2}	2.7×10^{-2}	3×10^{-1}	4.5×10^{-2}	9×10^{-4}
KH_2PO_4	uncertain	1.2×10^{-2}	—	4×10^{-2}	8×10^{-4}
K_2HPO_4	—	—	6.5×10^{-2}	4×10^{-2}	5×10^{-4}
$K_3P_4O_4$	—	—	4.5×10^{-2}	4.5×10^{-2}	—

* k_1, a rate constant corresponding to the increase of the polyphosphate fraction
** k_2, a rate constant corresponding to the increase of the orthophosphate fraction
*** k_3, a rate constant corresponding to the decrease of the polyphosphate fraction

follows the kinetics which contains several processes of the first order,[14] the rate constants for these processes can be defined. Since the rate is proportional to the number of species containing phosphorus-32, the formula, $dN_i/dt=k_iN_i$, expresses the process, where k_i is the rate constant for the change in the number of species and N_i is the number of species which contribute to the i-th process. The rate constant can be obtained at a fixed dose rate. The annealing curves were obtained for the several orthophosphate salts, and an analysis was made in order to estimate the rate constant from the numbers of the increases of the polyphosphates and orthophosphate, as Fig. 4 shows. In the case of polyphosphate, a correction was made for the contribution of the third process, which resulted in the slow decrease in the polyphosphate. The results obtained for the rate constants at given temperatures are shown in Table III. In the table, k_1 is the rate constant for the reduced species to the polyphosphate (process I) and k_2 is the rate constant for the reduced species to the orthophosphate (process II). In these estimates, samples were irradiated for 2 hr. in a pneumatic tube of the JRR-1. In order to estimate k_3, the rate constant for the polyphosphate to the orthophosphate (process III), samples were irradiated for 15 hr. in the vertical hole. In gamma irradiation at −50°C, only a slight change induced by this process is observed, even at the highest dose of 5×10^7 r. The rate constants obtained for sodium or potassium orthophosphates are of the order of $10^{-4}\,hr^{-1}$ (−50°C, 1.7×10^5 r./hr.). The rate constants obtained at 20°C are listed in Table III.

Similar experiments were made to estimate the rate constants for sodium pyrophosphate. The decrease in the reduced species uniquely follows the first-order kinetics, and the rate constant is 1.7×10^{-3} hr^{-1} (-50°C, 1.7×10^{5} r./hr.). This value is one order smaller than those for the orthophosphate salts.

The Effect of Temperature During Gamma Irradiation.—The temperature dependence of gamma-ray annealing is studied for all the salts mentioned. The decrease in the reduced species in sodium or potassium orthophosphates and in sodium pyrophosphate is clearly affected by the temperature during gamma irradiation. In Fig. 5, the decrease in the reduced species in sodium and potassium orthophosphate salts is plotted as a function of the total dose at 20°C. In the salts containing hydrogen atoms, the decrease in the reduced species is divided into two parts: the initial rapid decrease corresponding to processes I and II, and the slow decrease which is predominant in trisodium and tripotassium phosphates, as Fig. 5 shows. The former process is the same as that observed at -50°C. The decrease in the reduced species corresponds to the sum of the increases of the polyphosphate and orthophosphate. However, the latter slow process, which is not clearly observed at -50°C, is probably a different process from those mentioned above; it probably corresponds to the slow increase in the orthophosphate.

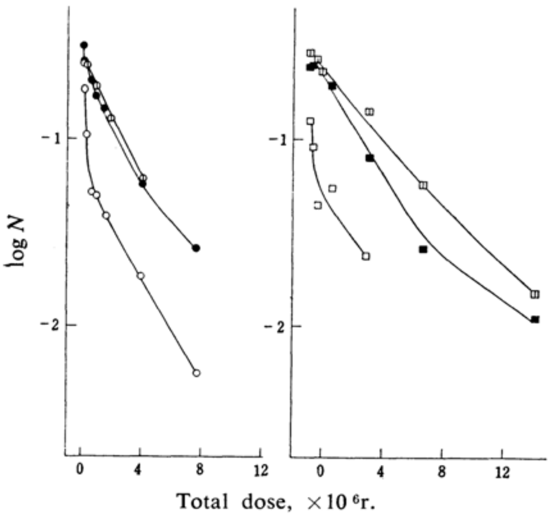

Fig. 5. Gamma ray annealing of ^{32}P species of the reduced species fraction for several orthophosphate salts.

—○—	NaH_2PO_4	—□—	KH_2PO_4
—●—	Na_2HPO_4	—■—	K_2HPO_4
—⦶—	Na_3PO_4	—◫—	K_3PO_4

The changes in the reduced species in disodium hydrogen phosphate at several different temperatures are shown in Fig. 6. In a series of the sodium orthophosphate salts and in a series of the potassium orthophosphate salts studied, the reduced species considerably decreased, even irradiation at -196°C. If the log k is plotted against $1/T$, the curve is quite different from the linear shape, where T is the absolute temperature. The log k decreases as the temperature is lowered to approximately -20°C, then it nearly approaches a constant at -196°C. The reaction induced by gamma irradiation at a low temperature seemed to involve another process. The process is apparently different from the higher temperature process above -20°C.

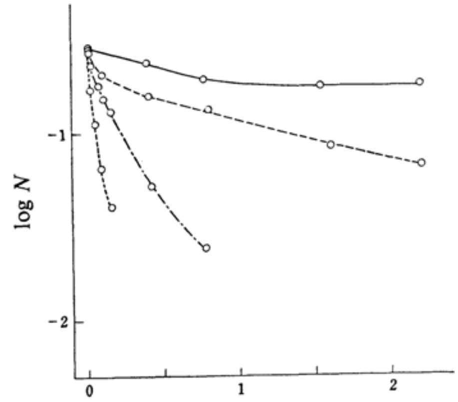

Fig. 6. Gamma ray annealing as functions of temperature during gamma ray irradiation—the decrease of ^{32}P for the reduced species fraction in disodium hydrogen phosphate.

—○—	at -196°C	—-○-—	at 20°C
--○--	at $-$ 50°C	----○----	at 100°C

Comparisons of Gamma-ray Annealing with the Chemical Form of the Samples.—From the comparison of the decreases in the reduced species by the gamma irradiation for the series of the orthophosphate salts, it is clear that the higher the hydrogen content in the sample, the greater the decrease in the reduced species.

Disodium hydrogen phosphate dodecahydrate was also studied. The change in the distribution of chemical species containing phosphorus-32 are similar to those in the anhydrous salt. The rate of decrease in the reduced species in sodium pyrophosphate is also affected by the temperature during gamma irradiation, whereas in sodium orthophophite and sodium hypophosphite, no change in chemical species by gamma irradiation is observed, even in irradiation at 20°C.

The rate-constant values obtained can not be compared in detail with the other observations in oxy-acid salts because the experimental conditions are different. However, the rate of the change of retention in orthophosphate salts is at least approximately 10^2 times greater than those in the other salts; namely, for bromine-82 in potassium bromate,[2] and chromium-51 in potassium chromate.[15]

From the results of the present experiment, it is to be expected that the neutron irradiation for relatively long periods of time or at high operating power will give the reduced species of low fractions in sodium or potassium orthophosphate salts.[8]

Summary

Radiation annealings with cobalt-60 gamma-rays have been investigated for several neutron-irradiated inorganic phosphorus compounds. The group separation technique by one-dimensional paper-partition chromatography was adopted to separate chemical species containing phosphorus-32. The reduced species in the sodium and potassium orthophosphate salts and in the sodium pyrophosphate salt decreased upon gamma irradiation, and an increase in the retention was observed. However, the polyphosphate increased initially in the several orthophosphate salts.

Three processes has been observed, the rate constants for these processes have been estimated, and two other processes have been suggested. The main process is the oxidation of the reduced species to phosphorus(V) species.

Radiation annealing have been studied for phosphates as a functions of the dose rate, the total dose of irradiation, and the temperature during gamma irradiation, it has been found that annealings are dependent upon the total dose and the temperature during irradiation and are independent of the dose rate. In orthophosphates and pyrophosphate, chemical species other than the parent species are easily annealed by gamma irradiation, whereas no detectable annealing has been observed in sodium orthophosphite or sodium hypophosphite.

In series of sodium and potassium orthophosphates, annealing was affected by the hydrogen content of the salts.

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15) G. Harbottle, *J. Chem. Phys.*, **22**, 1083 (1954).