The Szilard-Chalmers Reaction of Several Neutron-Irradiated Inorganic Phosphorus Compounds

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In 1948, Williams¹⁾ reported that, in the Szilard-Chalmers process, the longer the irradiation time in a reactor, the higher was the retention of the parent form for potassium ferrocyanide and antimony pentafluoride. This high retention for long irradiations was postulated as resulting from radiation annealing, particularly with gamma-rays.

In a series of studies by the author on the Szilard-Chalmers effects on several inorganic phosphorus compounds, such post-irradiation processes as thermal annealing²⁾ and gamma-ray annealing³⁾ were reported in the distribution of chemical species containing phosphorus-32 for several neutron-irradiated phosphates. In an experiment⁴⁾ concerned with the preparation of phosphorus-32 of a high specific activity by means of the (n, γ) reaction of phosphates, the recovery and enrichment factors were affected by the irradiation conditions.

In the present paper, studies will be made of the neutron irradiation of several phosphates under various irradiation conditions in order to find the optimum conditions of irradiation for the preparation of phosphorus-32 of a high specific activity. For the group separation of the chemical species of phosphorus-32, the results obtained by paper partition chromatography⁵⁾ will be compared with those obtained by the ion-exchange method and with those obtained by paper electrophoresis.⁶⁻⁹⁾ The effects of radiation in a reactor on the distribution of chemical species containing phosphorus-32 will also be discussed.

Experimental

Target Materials.—Guaranteed reagents were used without further purification. Hydrated salts were dehydrated, dried, and analyzed as previously reported.²⁾

Neutron Irradiation.—Samples sealed in a polyethylene tube were irradiated in the holes of JRR-1 (operated at 40 kW.) or of JRR-2 (operated at 5 MW.). Thin gold foils were used as thermal neutron flux monitors, and thin aluminum foils and small nickel pellets, as fast neutron flux monitors. These monitors were irradiated by being placed in a capsule holding the target material. When irradiated in a glory hole of JRR-1 and in a vertical hole of JRR-2, the samples were sealed in a quartz tube which was then placed in an aluminum container. The samples were irradiated at ambient reactor temperatures.

Separation Procedure.—After irradiation, the samples were stored in a vessel cooled with dry ice. Each sample was then dissolved in water so that the concentration was made 0.1 M. The solution was submitted to one-dimenssional paper partition chromatography. Two different systems were used for the separation; one used *n*-butanol saturated with 2 N nitric acid as the developing agent, and the other, a mixture of 1 N ammonia, dioxane and *n*-butanol (1 : 1 : 1, volume ratio). The

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1) R. R. Williams, *J. Phys. Colloid Chem.*, **52**, 603 (1948).

2) H. Baba, K. Tanaka and K. Yoshihara, This Bulletin, **36**, 928 (1963).

3) K. Tanaka, ibid., **37**, 1032 (1964).

4) K. Tanaka, to be published.

5) K. Yoshihara and T. Yokoshima, This Bulletin, **34**, 123 (1961).

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

7) T. R. Sato, P. A. Sellers and H. H. Strain, ibid., **11**, 84 (1959).

8) T. R. Sato, *Anal. Chem.*, **31**, 841 (1959).

9) H. Michl, *J. Chrom.*, **1**, 93 (1958).

TABLE I. THE DISTRIBUTION OF CHEMICAL SPECIES CONTAINING PHOSPHORUS-32 FOR DISODIUM HYDROGEN PHOSPHATE: COMPARISON OF THREE SEPARATION METHODS

By paper partition chromatography	%	By paper electrophoresis	%	By ion exchange method	%
Polyphosphates	46.1	Polyphosphates	45.0	Fraction absorbed with an aqueous chlorides solution	62.2
		Isohypophosphate and hypophosphate	18.4		
Orthophosphate	22.0	Orthophosphate	23.1	Fraction eluted with an aqueous chlorides solution	37.8
		Orthophosphite	9.9		
Reduced species	32.0	Hypophosphite	3.6		
(P(I)	2.9)				

procedure was the same as has previously been described.[2] The ion exchange method used to prepare phosphorus-32 of a high specific activity was also the same as in a previous paper.[4] When the sample solution in an equimolar mixture of 0.025 M potassium chloride and 0.025 M hydrochloric acid was passed through the column, orthophosphate, orthophosphite, and hypophosphite ions were eluted with an equimolar mixed solution of 0.025 M potassium chloride and 0.025 M hydrochloric acid, and the absorbed phosphorus-32 was completely eluted with 8 M hydrochloric acid. The distribution of the chemical species containing phosphorus-32 formed in phosphates by neutron irradiation was very complex; therefore, the distribution of the phosphorus oxy-acid species obtained by the two methods were compared with that obtained by paper electrophoresis. Recently, the usefulness of high voltage electrophoresis for the separation of a complex phosphate mixture has been recognized; in such an electrophoresis voltage gradients up to 80 V./cm. were attained. Lindner and Harbottle[10] applied this method to finding the distribution of the chemical species containing phosphorus-32 in neutron irradiated phosphates. In the present experiment, the sample was dissolved in 0.1 M lactic acid, and a 0.1 M lactic acid solution was used as the electrolyte. The voltage gradient was 80 V./cm. During development, the filter paper (Whatman 3 MM) was clamped between two glass plates, the upper plate being cooled with ice. The separation took about one hour.

Counting Procedure.—After separation, the filter paper was dried and cut into pieces 1 cm. wide. These pieces were placed on the bottom of a glass planchet (2.5 cm. in diameter) and counted with a gas-flow GM counter, an automatic sample changer made by the Tracer-Lab Inc. also being used. Each piece was counted at least ten days after neutron irradiation to avoid error arising from contamination by sodium-24 or potassium-42. The total count was 2^{10} counts for each piece. The sample in a solution was evaporated in a glass planchet (2.5 cm. in diameter) and counted with a thin end-window-type gas flow GM counter. The gamma-ray spectra were measured with a 256-channel scintillation spectrometer equipped with a NaI crystal (7.4 cm. × 7.4 cm.).

The Chemical Analysis of Phosphorus.—Trace amounts of phosphorus were determined by colorimetry, as has been reported by Gaitanis.[11] For macroamounts, gravimetric determination was used after precipitating the phosphorus with ammonium molybdate.

Results and Discussion

The distribution of the chemical species containing phosphorus-32 was studied using the three different separation methods described above, and the distributions were compared with each other. Each sample was irradiated for 2 hr. in a pneumatic tube of JRR-1 (the nominal neutron flux, 0.64×10^{12} n./cm^2-sec). The results obtained for disodium hydrogen phosphate are shown in Table I. In all three separations the storage time was also the same. In the paper partition chromatography, three fractions, the polyphosphates, the orthophosphate and the reduced species, were separated. The polyphosphates and the reduced species consisted of mixed phosphorus oxy-acid species, as has previously been reported.[2] From the analysis of the R_f values, tripolyphosphate and pyrophosphate were observed in the chromatographic histogram for the polyphosphates. Hypophosphite was observed by separation with a mixture of 1 N ammonia, dioxane and *n*-butanol. As may be seen in the table, the percentages of phosphorus-32 in the polyphosphates and in the orthophosphate are the same as those obtained by the paper electrophoresis. On the other hand, the percentage of the reduced species is much larger than the sum of the orthophosphite and hypophospphite given by the paper electrophoresis. This difference corresponds exactly to the percentages of the isohypophosphate and hypophosphate in the paper electrophoresis.

In the ion exchange separation, the activities of the fractions which are absorbed on the anion exchange resin from the aqueous chloride

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[10] L. Lindner and G. Harbottle, "Proceedings of Chemical Effects of the Nuclear Transformations," Vol. I, IAEA, Prague (1961), p. 485.

[11] M. J. Gaitanis, "Master Analytical Manual," Section 1-12 TID-7015 (1957).

solutions are higher than those of the polyphosphates obtained by the other separations. In the case of the ion exchange separation, the elutions were made successively with a potassium chloride solution, as has been reported by Weiser.[12] Appoximately one-half of the total activity of the absorbed fraction is found in pyrophosphate and tripolyphosphate; the remaining half is not identified. The percentages of the sum of the polyphosphates, isohypophosphate and hypophosphate in the paper electrophoresis were approximately equal to those absorbed on the anion exchange resin. For the neutron-irradiated orthophosphate salts treated with anion exchange resin, the eluted solution with 8 M hydrochloric acid was evaporated to near dryness by heating the solution and submitting it to one-dimenssional paper partition chromatography. Phosphorus-32 was observed in the orthophosphate and reduced species. Because orthophosphite and hypophosphite ions were eluted with an aqueous chloride solution, this provided other evidence that the reduced polyphosphate species were formed by the Szilard-Chalmers process of orthophosphate salts. These species were absorbed on the resin from the aqueous chloride solutions.

Several orthophosphate salts, sodium orthophosphite and sodium hypophosphite were irradiated in a pneumatic tube of JRR-1. The distribution of the chemical species containing phosphorus-32 which was obtained by paper partition chromatography is plotted in Fig. 1—3 as a function of the neutron irradiation time. For the orthophosphate salts, the shorter the irradiation time, the higher was the percentage of the reduced species, but the lower were those of the polyphosphates and orthophosphate. The fraction of orthophosphate is considerably reduced by irradiating it for shorter periods of time. However, the distribution of the phosphorus oxy-acid species contaianing phosphorus-32 was apparently independent of the irradiation time for sodium orthophosphite and sodium hypophosphite, although the fraction of hypophosphite in sodium orthophosphite slightly decreases when the sample is irradiated for longer periods of time.

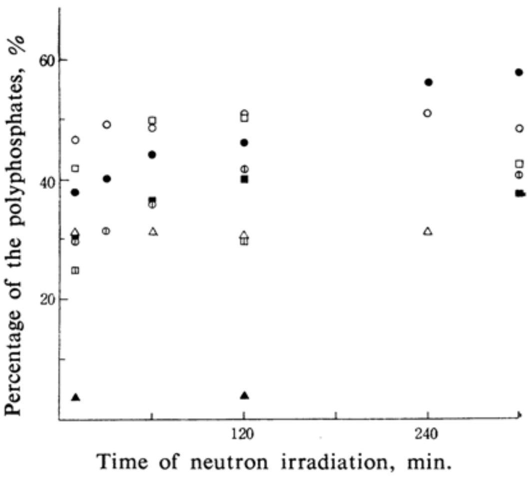

Fig. 1. The polyphosphates as a function of irradiation time.
○ Sodium dihydrogen phosphate
● Disodium hydrogen phosphate
⦶ Trisodium phosphate
□ Potassium dihydrogen phosphate
■ Dipotassium hydrogen phosphate
◫ Tripotassium phosphate
△ Sodium orthophosphite
▲ Sodium hypophosphite

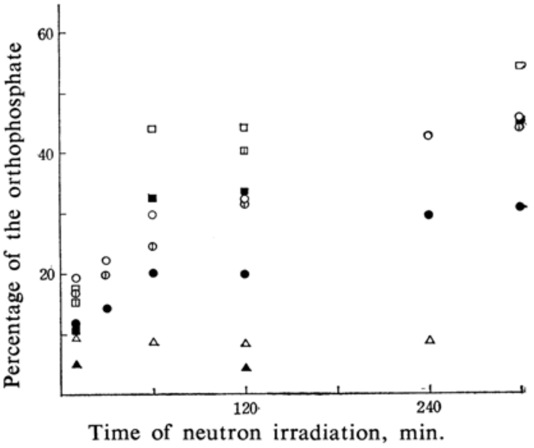

Fig. 2. The orthophosphate as a function of irradiation time.
○ Sodium dihydrogen phosphate
● Disodium hydrogen phosphate
⦶ Trisodium phosphate
□ Potassium dihydrogen phosphate
■ Dipotassium hydrogen phosphate
◫ Tripotassium phosphate
△ Sodium orthophosphite
▲ Sodium hypophosphite

The samples were irradiated at various locations in the reactor of JRR-1. The results obtained from these irradiations are shown in Table II. The thermal neutron fluxes measured with a thin gold foil by a calibrated ionization chamber are shown in the third column in Table II. The fast neutron fluxes in the fourth column were obtained from the induced activity of magnesium-27 by the $^{27}Al(n, p)^{27}Mg$ reaction, assuming that the cross section was 3.1 millibarns.[13] The energy distribution of the fast neutrons at any location in a reactor was assumed to be the same as that of the

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[12] H. J. Weiser, Jr., *J. Am. Oil Chemists Soc.*, **34**, 124 (1957).

[13] J. C. Roy and J. J. Hawton, CRC-1003 (1960).

TABLE II. THE DISTRIBUTION OF CHEMICAL SPECIES CONTAINING PHOSPHORUS-32 ON IRRADIATION AT VARIOUS LOCATIONS IN JRR-1

Neutron irradiation		Thermal neutron	Fast neutron	Gamma ray	Polyphosphates	Orthophosphate	Reduced species
Hole	Time	n./cm²-sec.	n./cm²-sec.	r./hr.	%	%	%
			NaH_2PO_4				
No. 1	10 min.	1.2×10^{12}	1.2×10^{12}	1.3×10^{7}	59.6	31.4	9.0
No. 2	10 min.	4.2×10^{11}	3×10^{10}	2×10^{6}	48.9	23.3	27.9
No. 3	10 min.	3.9×10^{11}	7.7×10^{10}	1×10^{6}	48.4	21.4	30.3
No. 12	10 min.	3.5×10^{11}	10^{9}	4.5×10^{5}	39.2	24.1	36.7
No. 1	5 hr.	1.2×10^{12}	1.2×10^{12}	1.3×10^{7}	36.9	63.1	0.0
			Na_2HPO_4				
No. 1	10 min.	1.2×10^{12}	1.2×10^{12}	1.3×10^{7}	64.5	16.2	19.3
No. 2	10 min.	4.2×10^{11}	3×10^{10}	2×10^{6}	32.7	15.9	51.4
No. 3	10 min.	3.9×10^{11}	7.7×10^{10}	1×10^{6}	33.4	16.1	50.5
No. 12	10 min.	3.5×10^{11}	10^{9}	4.5×10^{5}	38.4	14.9	46.7
No. 1	5 hr.	1.2×10^{12}	1.2×10^{12}	1.3×10^{7}	53.9	45.9	0.2
			KH_2PO_4				
No. 1	10 min.	1.2×10^{12}	1.2×10^{12}	1.3×10^{7}	51.5	36.0	12.4
No. 12	10 min.	3.5×10^{11}	10^{9}	4.5×10^{5}	32.1	25.7	42.2
No. 1	5 hr.	1.2×10^{12}	1.2×10^{12}	1.3×10^{7}	19.4	80.3	0.3

TABLE III. THE DISTRIBUTION OF CHEMICAL SPECIES CONTAINING PHOSPHORUS-32 OBTAINED BY IRRADIATION IN A PNEUMATIC TUBE OF JRR-1* AND OF JRR-2** for 20 min.

Target material	Polyphosphates, %		Orthophosphate, %		Reduced species, %	
	JRR-1	JRR-2	JRR-1	JRR-2	JRR-1	JRR-2
NaH_2PO_4	47.2	51.4	20.8	46.4	31.8	2.2
Na_2HPO_4	39.0	56.4	14.5	32.7	46.5	11.4
KH_2PO_4	45.8	41.6	26.0	56.4	28.0	1.9
K_2HPO_4	32.0	43.0	14.3	46.7	53.6	10.3
K_3PO_4	25.7	38.2	19.2	43.2	55.0	18.6

* Thermal neutron flux, 5.0×10^{11} n./cm²-sec.
Fast neutron flux, 6.0×10^{10} n./cm²-sec.
** Thermal neutron flux, 3.0×10^{13} n./cm²-sec.
Fast neutron flux, 1.0×10^{12} n./cm²-sec.
Gamma flux, $\sim1\times10^{8}$ r./hr. (JAERI Memo, No. 1098 (1963))

fission neutrons.[14,15] The fast neutron fluxes obtained by this reaction were checked by those from other reactions, $^{27}Al(n, \alpha)^{24}Na$ and $^{58}Ni(n, p)^{58}Co$.

At the central position in the glory hole of JRR-1 at 40 kW. operation, the fast neutron flux obtained by this method agreed with other observations,[16] $1.2\sim1.5\times10^{12}$ n./cm²-sec. For the gamma-ray intensity in the reactor, the data shown by Nakadoi et al.[17] were used. When irradiated for the same period of time, the distribution of the chemical species containing phosphorus-32 was strongly dependent on the location where they were irradiated. For sodium dihydrogen phosphate, the reduced species obtained by irradiation in the glory hole considerably differed from those of the other locations. The reduced species in two different salts were compared. The percentages of the reduced species in the sodium dihydrogen phosphate salt and in the disodium hydrogen phosphate salt were approximately the same when irradiated in the vertical hole No. 12; however, the percentage of the reduced species in the disodium hydrogen phosphate salt was approximately twice that in the sodium dihydrogen phosphate salt when irradiated in the glory hole.

The orthophosphate salts were irradiated in a pneumatic tube of JRR-2 (operated at 5 MW). The distributions obtained by the chromatographic separation were compared with those of JRR-1 as shown in Table III. Low proportions of the reduced species were observed when they were irradiated at a high operating

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[14] T. O. Passell and R. L. Heath, *Nucl. Science and Engineering*, **10**, 309 (1961).
[15] B. E. Watt, *Phys. Rev.*, 57, 1037 (1952).
[16] H. Ezure et al., private communication.
[17] S. Nakadoi et al., private communication.

TABLE IV. ENRICHMENT OF PHOSPHORUS-32 BY ION EXCHANGE SEPARATION USING JRR-2

Target material	Neutron irradiation		Thermal neutron flux (n./cm^2-sec.)	Recovery %	Enrichment factor
	Hole	Time			
KH_2PO_4	Pneumatic tube	20 min.	9.4×10^{12}	55.2	1.7×10^4
KH_2PO_4	Vertical hole	50 hr.	6.2×10^{12}	14.0	8.0×10^3
NaH_2PO_4	Vertical hole	72 hr.*	2.5×10^{13}	30.1	0.95
Na_2HPO_4	Vertical hole	72 hr.	2.5×10^{13}	66.9	1.3

* Ambient reactor temperature at 170°C.

TABLE V. THE APPARENT RATE CONSTANTS FOR THE VARIATION OF THE ORTHOPHOSPHATE AND FOR THOSE OF THE REDUCED SPECIES

Irradiation conditions			Apparent rate constants, hr^{-1}				Ratio of the apparent rate constants between two salts $k_{(NaH_2PO_4)}/k_{(Na_2HPO_4)}$	
			Orthophosphate		Reduced species			
Reactor	Hole	Time	NaH_2PO_4*	Na_2HPO_4*	NaH_2PO_4	Na_2HPO_4	Orthophosphate	Reduced species
JRR-1	No. 1	10 min.	9.0	15	36	18	0.6	2.0
JRR-1	No. 2	10 min.	3.5	4.0	9.0	1.7	0.9	5.2
JRR-1	No. 3	10 min.	2.5	4.1	7.7	1.8	0.6	4.3
JRR-1	No. 12	10 min.	3.8	3.2	4.8	2.8	1.2	1.7
JRR-1	No. 16	10 min.	1.4	1.4	5.9	2.0	1.0	3
JRR-2	pneumatic tube	20 min.	14	9.3	73	14	1.5	5.2

* Sample salts tested.

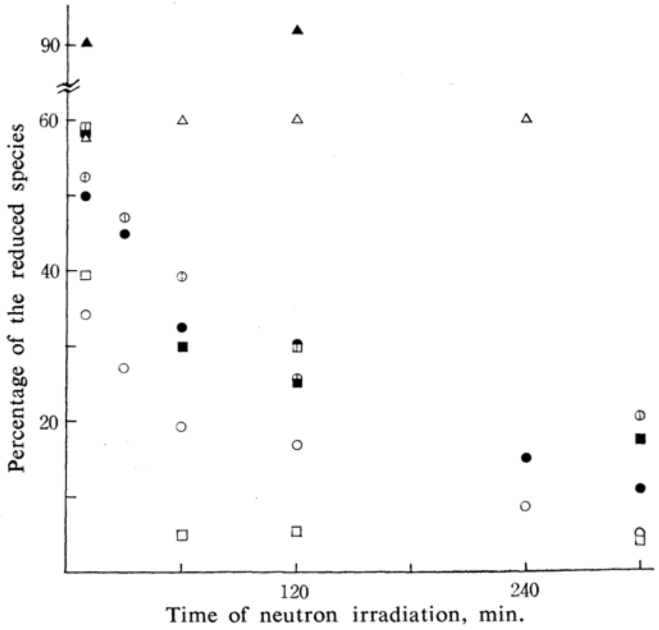

Fig. 3. The reduced species as a function of irradiation time.

○ Sodium dihydrogen phosphate
● Disodium hydrogen phosphate
⦶ Trisodium phosphate
☐ Potassium dihydrogen phosphate
■ Dipotassium hydrogen phosphate
⊞ Tripotassium phosphate
△ Sodium orthophosphite
▲ Sodium hypophosphite

power. This is due to the greater dose exposures in the reactor. Some of the orthophosphate salts were irradiated in a vertical hole of JRR-2 and subjected to ion exchange separation. Decreases in the recovery were observed for longer periods of irradiations, as Table IV shows. When the salts were neutron-irradiated for 72 hr. at ambient reactor temperatures up to 170°C in a vertical hole of JRR-2 for sodium dihydrogen phosphate and disodium hydrogen phosphate, the enrichment factor decreased to approximately unity. This can be explained by the thermal pyrolysis of the orthophosphate salts. The ambient reactor temperature was measured with a very thin (0.3 mmϕ) alumelchromel thermo-couple placed adjacent to the sample. The low fractions of the polyphosphates in Table IV are the results for irradiations at high ambient reactor temperatures. They can be attributed to the effects not only of radiation annealing but also of thermal annealing.

When the irradiation time was extrapolated to zero, the retention as orthophosphate approached approximately 8 to 15% for the orthophosphate salts studied. Although this retention was obtained for irradiation at ambient reactor temperatures of JRR-1, much difference was not seen between the retention estimated by the extrapolation of the irradiation time to zero and those obtained by irradiation cooled with liquid nitrogen for 2 hr.[18]. This suggests that the distribution of the chemical species containing phosphorus-32 at an irradiation time of zero, which is called the initial distribution, is independent of such post-irradiation effects as thermal and radiation annealing.[3]

As the chemical species were annealed by gamma irradiation, an attempt was made to analyze the variation of the distribution of the chemical species with the neutron irradiation time[1] in a reactor. On irradiation in JRR-1, the effect of radiation annealing would be the greatest cause of the variation of the distribution, because ambient reactor temperatures were not so high[19] that the thermal annealing was prominent for the variation of the distribution. Roughly speaking, if the rate of the annealing of the chemical species containing phosphorus-32 is proportional to the numbers of the chemical species present, the apparent rate constant is dependent on the intensity of radiation in a reactor; then

$$N_t = N_0 \frac{\lambda}{\lambda+k}\left[\frac{1-\exp\{-(\lambda+k)t\}}{1-\exp(-\lambda t)}\right]$$

where k is the apparent rate constant for the variation of the distribution, λ is the decay constant of phosphorus-32, and N_0 and N_t are the numbers of the chemical species at irradiation time zero and at irradiation time t respectively. For this analysis, the initial distribution was assumed to be independent of the post-irradiation effects. For the initial distribution, N_0, the extrapolated values at irradiation time zero for the reduced species were used. However, those for the polyphosphates and orthophosphate were estimated in a different way because these fractions increased with the increase of neutron irradiation time, and the sum of the increase of these two fractions corresponded to the decrease of the reduced species. At an infinitely long irradiation time, N_t approached a constant value; namely, $N_{t=\infty} = \lambda/(\lambda+k)$. If $k \gg \lambda$ were attained as expected from the results of the radiation-annealing experiment, this value might be assumed to be zero at a long irradiation time. The difference between the numbers of the polyphosphates obtained by a 5 hr.-neutron irradiation of JRR-1 and those of the fraction at irradiation time zero was assumed to be the initial distribution of the annealable species in the increase of the polyphosphates. The remaining fraction of the reduced species was then assigned to be the initial distribution of those in the increase of the orthophosphate.

The estimation of the apparent rate constants is based on the best fit of each experimental value, N_t at irradiation time t. The apparent rate constants are shown in Fig. 1, where the neutron irradiation time is shown on the absissa. The apparent rate constants thus

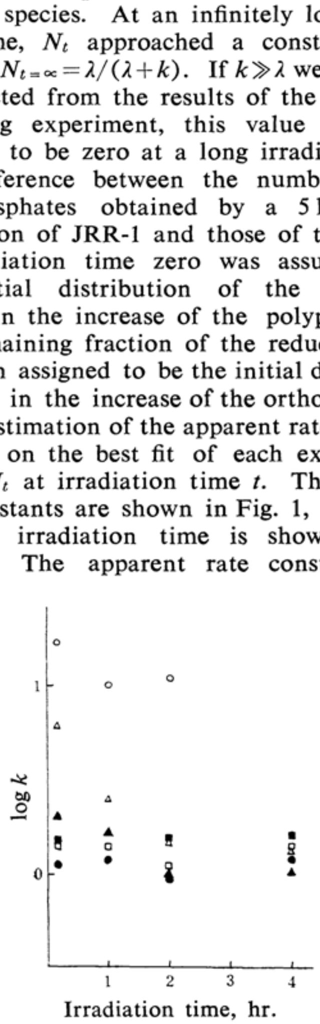

Fig. 4. The apparent rate constants.
Polyphosphate
○ NaH_2PO_4 ● Na_2HPO_4
Orthophosphate
□ NaH_2PO_4 ■ Na_2HPO_4
Reduced species
△ NaH_2PO_4 ▲ Na_2HPO_4

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[18] R. F. C. Claridge and A. G. Maddock, *Trans. Faraday Soc.*, **59**, 935 (1963).

[19] K. Tomabechi, private communication.

obtained for the variation of the reduced species vary with the neutron irradiation time; the shorter the irradiation time, the higher the apparent annealing rate. However, this is to be expected from the finding that the radiation annealing takes place by means of mixed processes for the reduced species, as was shown in a previous paper.[3] In the increase of the orthophosphate, however, the apparent rate constants seemed to be independent of the neutron irradiation time. The results shown in Table II and Table III were also analyzed for sodium dihydrogen phosphate and disodium hydrogen phosphate. The ratio between the apparent rate constants for the two salts is compared with different locations on irradiation. This is shown in Table V. The apparent rate constants change roughly with the pile factor, and the ratio of these constants for the two salts seemed to fluctuate independent of the irradiation conditions. The effects of fast neutrons in a reactor were probably suggested by the ratio of these rate constants among the salts in which the hydrogen content was a variable, because the effective dose was attributed to the hydrogen atoms in the salts. The does rates were estimated from the results of fast neutron fluxes obtained above. For this estimation, it was assumed that the energy distribution was the same as that of fission neutrons, and that all the energies of the scattered atoms were absorbed into the sample. It was approximately one-fourth of the gamma ray dose intensity for dihydrogen phosphate and one-twentieth of that for monohydrogen phosphate at the maximum (No. 1 hole of JRR-1). However, the ratio was not increased. Fast neutrons were probably less effective for the annealing process during irradiation in a reactor.

Summary

The distribution of the chemical species containing phosphorus-32 formed by the (n, γ) reaction has been studied for several phosphates as functions of the irradiation conditions in a reactor. The variation in the distribution has been discussed in connection with the radiation annealing process during irradiation, and a comparison of the distribution of the chemical species containing phosphorus-32 by three separation methods has been made.

By means of the analysis of the variation curves of the distribution of the chemical species containing phosphorus-32, the apparent rate constants have been estimated. It has been suggested that the variations in the distribution may be approximately expressed by radiation annealing processes, and that they are affected by pile factors.

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