Studies on the Chemical Forms of the Recoil Products in Some Neutron-Irradiated Phosphorus Compounds

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The Szilard-Chalmers effect in the neutron-irradiated phosphorus compounds is rather complicated. This phenomenon was studied by several authors, but some important problems seem to be still left without any clear solution. In 1940, Libby[1] studied the Szilard-Chalmers effect in phosphate and phosphite, and found that phosphite is formed in neutron-irradiated phosphate. The retention of phosphate was about 50%. Thomas et al.[2] studied similar effects. In 1951, Fiskell[3] discovered some formation of hypophosphite in neutron-irradiated phosphate.

Fiskell et al.[4] continued further investigation on the Szilard-Chalmers effect of calcium phosphates, and found that pyro- and metaphosphate are formed besides hypophosphate. Aten et al[5]. also investigated the formation of the polyatomic species in several neutron-irradiated phosphorus compounds, and demonstrated the presence of pyrophosphate in the recoil products. In the papers mentioned above the precipitation method was used for the analysis of the irradiated phosphorus compounds, and therefore exact determination of the complicated products was difficult.

Recently, the technique of paperelectrophoresis has been developed and has been applied successfully to the separation of many components in the complicated system. Sellers et al.[6] studied the chemical form of the recoil products in various phosphorus compounds by this method. Sato et al.[7] further investigated the question in the same way. These authors[6,7] reported that the principal component in each case was the parent species, and besides this principal component several components appeared in the chromatogram in small percentages. They argued that neutron-irradiation of various phosphates does not bring about extensive disruption of the P–O bonds or the P–O–P linkage.

Although paper electrophoresis is an excellent method for the separation and the determination of various phosphorus compounds, it

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1) W. F. Libby, *J. Am. Chem. Soc.*, **62**, 1930 (1940).
2) W. D. E. Thomas and D. J. D. Nicholas, *Nature*, **163**, 719 (1949).
3) J. G. A. Fiskell, *Science*, **113**, 244 (1951).
4) J. G. A. Fiskell, W. A. Delong and W. F. Oliver, *Can. J. Chem.*, **30**, 9 (1952).
5) A. H. W. Aten, Jr., H. van der Straaten and P. C. Riesbos, *Science*, **115**, 267 (1952).
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., **7**, 84 (1959).

should be limited to the analysis of the species which are stable to the electric current and to the heat liberated on the paper for several hours. Therefore we felt it would be necessary to compare the results with those by ordinary paper chromatography. We were particularly interested in the formation of polyatomic species which might be produced by the heat liberated in the neighborhood of the recoil atom. Sato et al.[7] detected a component presumably corresponding to pyrophosphate in neutron-irradiated phosphate, but they did not show the percentage of this component. Aten et al.[5] showed that an appreciable fraction of pyrophosphate is formed from phosphate. However, the formation of higher polyphosphates than pyrophosphate might occur, but this has not been shown so far. Thus we studied the chemical form of the recoil products in the neutron-irradiated phosphorus compounds by paper chromatography, and found several new facts.

Experimental

Target Materials.—The target materials used in this work are as follows: H_3PO_4; NaH_2PO_4, $NaH_2PO_4 \cdot H_2O$, $NaH_2PO_4 \cdot 2H_2O$, $NH_4H_2PO_4$, KH_2PO_4, Na_2HPO_4, $Na_2HPO_4 \cdot 12H_2O$, $(NH_4)_2HPO_4$; Na_3PO_4, $Na_3PO_4 \cdot 12H_2O$, $Zn_3(PO_4)_2$; $Na_4P_2O_7$, $Na_4P_2O_7 \cdot 10H_2O$; $Na_2HPO_3 \cdot 5H_2O$.

These substances are guaranteed reagents of the Kanto Chemical Co. or of the Wako Pure Chemical Ind. Before the experiment the purity of each substance was tested by means of radioactivation analysis; the sample was dissolved in water (zinc phosphate was dissolved in dilute hydrochloric acid), and one drop of the solution was put on the filter paper for chromatography; this was developed with *n*-butanol which had been shaken with the same volume of 2 N nitric acid; the filter paper was dried and irradiated in a nuclear reactor; after appropriate cooling time, the radioautogram of the filter paper was prepared. Each test gave no impure component.

Irradiation.—Solid targets were irradiated in the Irradiation Hole No. 3, 12 or 15 in the nuclear reactor JRR-1 (homogeneous solution type). Hole No. 16 was used for short irradiation of solid targets. Liquid targets were irradiated in Hole No. 6. The standard thermal neutron flux in each hole is given as follows[8].

No. 3.	0.48×10^{12} n/cm²/sec.
6.	0.40 〃
12.	0.38 〃
15.	0.22 〃
16.	0.51 〃

These values were given at the operation of 40 kW. per hour. In the whole period of this work the reactor was operated at 40 kW. per hour. It is desirable to irradiate the sample in the same position of the same hole, but this could not be realized for all cases. Presumably the variation of neutron flux in these experiments will not bring about any difference in the results. In Hole No. 16 (the nearest from the reactor core) the contribution of fast neutrons to the total radioactivation was tested by the cadmium foil absorption method. The result showed that about 5% of the radioactivity was produced by fast neutrons (residual 95% by slow and thermal neutrons). In the other holes contribution of neutrons to the total radioactivation will be smaller. Perhaps the contribution of fast neutrons will not greatly affect the results in all the experiments. Except in the case of short irradiation, the targets were usually irradiated for 5 hr. a day, and for successive three days a week. The irradiation temperature did not exceed about 50°C in any of the experiments.

Analysis.—*Paper chromatography.*—The irradiated target was dissolved in water, and one drop of the solution was put on the starting point of the filter paper, Tôyô No. 53 (2 cm × 40 cm). Other sorts of filter paper such as Tôyô No. 50, 51, 51A, 52 and 54 were tested, but No. 53 gave the best results. Several developing solvents were tested, and the best results were obtained by the use of *n*-butanol which had been shaken with the same volume of 2 N nitric acid. Development was made by the one-dimensional ascending method for about 15 hr., the travelling distance being 23~27 cm.

Detection of Radioactive Zones. — After development the filter paper was dried well and the radioautogram was taken on Fuji X-ray film. For the determination of the components on the chromatogram, the paper was cut in sections of 0.5 cm. width, and the radioactivity was measured by a proportional counter (Radiation Counter Laboratories, Inc.; an end-window type; flow gas, methane; counting efficiency about 30%,). When other radionuclides such as ^{24}Na and ^{42}K were produced, decay curves were investigated to distinguish them from ^{32}P.

Miscellaneous.—Experiments on the time-dependency of ^{32}P were carried out at room temperature (about 20°C) in air (under atmospheric pressure). Enrichment of ^{32}P was roughly examined by the coloration test on the chromatogram obtained. A solution of ammonium molybdate was sprayed on the filter paper. In the cases of phosphate, pyrophosphate and higher polyphosphates a yellow color appeared, and in the cases of phosphite and hypophosphite a pale blue color appeared after the filter paper was heated. Thus amounts of the phosphorus compounds were roughly estimated.

Result

There were small changes in R_f values according to the experimental condition, but they did not exceed 0.02. In Fig. 1, chromatograms of several species are shown. The R_f values of phosphate, phosphite* and pyrophosphate

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[8] K. Takahashi, M. Imai and Y. Kato, *JAERI-1004* (1958).

* The R_f value of hypophosphite is nearly the same as that of phosphite and they could not be distinguished from each other. The sum of these fractions are shown in the tables.

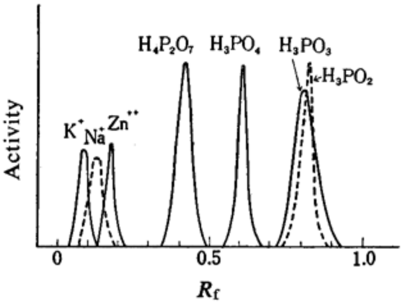

Fig. 1. R_f values of some phosphorus compounds.

were referred to in each experiment. In some cases an unknown species was developed at an R_f value of 0.95~1.0. This was usually observed as a very small spot. In almost all the experiments, spots appeared at the R_f value of 0.05~0.4. Usually these were not clear but diffused and trailing. Sometimes two or three spots appeared in these parts. On the other hand, when a disodium hydrogen phosphate sample was heated and dehydrated into pyrophosphate and higher polyphosphate, this sample always showed the spots at the R_f value of 0.05~0.4 besides a spot of pyrophosphate. Moreover, trimetaphosphate and hexametaphosphate were developed at the R_f value of 0.05~0.1. Therefore the spots at the R_f value of 0.05~0.4 were considered to be due to higher polyphosphates. In some experiments a spot appeared at the starting point of the chromatogram. This small fraction seems to be due to elementary phosphorus as was suggested by previous authors[6,7]. Oxidation of phosphorus might occur because the targets were irradiated in air. In the tables the sum of the percentages of the fractions is not always 100%, because the fractions of the tailing part of each spot, of the spot at the starting point, and of the spot at the R_f value of 0.95~1.0 are omitted. Errors shown in the tables include not only counting errors but errors based on incomplete separation of the spots.

The enrichment of ^{32}P was examined by the coloration already mentioned. Except for the target compound the chemical species which appeared in the chromatogram were not detected by the test. Comparing it with the radioactivity data in the tables, this result shows that the chemical species other than the target compound are enriched by the Szilard-Chalmers effect.

The test for radioactive gases such as phosphine and diphosphine was omitted in this work. As shown in Sellers's work[6] these were present only in a very small percentage.

Phosphoric Acid. — Liquid phosphoric acid was irradiated in Hole No. 6 (neutron flux: 0.40×10^{12}n/cm^2/sec.) in JRR-1 for 5 hr. The results are shown in Table I. Small changes in the distribution are observed with the time elapsed. Most of ^{32}P atoms are present as phosphoric acid, and small portions are present as phosphorous and pyrophosphoric acids. Phosphorous acid and pyrophosphoric acid seem to change slowly into phosphoric acid. Besides these, higher polyphosphates fractions were detected.

Potassium Dihydrogen Phosphate.—The target was irradiated in Hole No. 15 (neutron flux: 0.22×10^{12}n/cm^2/sec.) in JRR-1 for 15 hr. The results are shown in Table II.

In this experiment higher polyphosphates

TABLE I. SZILARD-CHALMERS EFFECT IN PHOSPHORIC ACID

Chemical forms of ^{32}P	Time elapsed after irradiation (days)			
	1	5	8	15
	%	%	%	%
H_3PO_4	89.2±0.4	92.6±0.5	93.9±0.5	95.7±0.5
$H_3PO_3(+H_3PO_2)$	5.1±0.1	2.9±0.06	2.2±0.06	0.3±0.01
$H_4P_2O_7$	2.5±0.07	1.4±0.04	1.2±0.04	1.0±0.04
Higher polyphosporic acid	2.0±0.09	Trace	Trace	Trace

TABLE II. SZILARD-CHALMERS EFFECT IN POTASSIUM DIHYDROGEN PHOSPHATE

Chemical forms of ^{32}P		Time elapsed after irradiation (days)		
		7	14	26
		%	%	%
Phosphate		43.5±0.4	43.7±0.4	45.4±0.5
Phosphite (+hypophosphite)		13.9±0.3	13.2±0.3	13.1±0.3
Pyrophosphate		11.8±2.0	14.7±2.6	15.2±2.6
Higher polyphosphates	R_f 0.09	19.6±3.3	9.6±1.6	21.5±3.7
	Others	9.9±3.2	14.9±4.8	4.5±1.5

Table III. Szilard-Chalmers effect in ammonium dihydrogen phosphate

Chemical forms of ^{32}P	Time elapsed after irradiation (days)			
	Sample I	Sample II		
	0	5	7	17
	%	%	%	%
Phosphate	47.8±0.7	54.1±0.8	56.4±0.9	55.9±0.8
Phosphite (+hypophosphite)	13.1±0.6	7.1±0.3	6.2±0.3	6.5±0.3
Pyrophosphate	8.4±1.6	18.1±2.8	15.0±2.8	15.3±2.8
Higher polyphosphates R_f 0.09	29.3±4.8	12.7±2.8	8.7±1.9	17.4±2.9
Higher polyphosphates Others		7.0±3.6	13.5±7.0	

Table IV. Szilard-Chalmers effect in $NaH_2PO_4 \cdot 2H_2O$

Chemical forms of ^{32}P	Time elapsed after irradiation (days)			
	4	6	8	10
	%	%	%	%
Phosphate	78.2±0.6	83.5±0.7	83.0±0.7	77.8±0.6
Phosphite (+hypophsphite)	2.4±0.1	—	—	—
Pyrophosphate	16.8±2.0	9.9±1.2	9.9±1.2	11.7±1.4
Higher polyphosphates	2.4±0.2	6.5±0.7	6.9±0.7	10.4±1.0

Table V. Szilard-Chalmers effect in $NaH_2PO_4 \cdot H_2O$

Chemical forms of ^{32}P	Time elapsed after irradiation (days)
	4
	%
Phosphate	78.6±1.3
Phosphite (+hypophosphite)	4.7±0.2
Pyrophosphate	8.6±1.9
Higher polyphosphates	7.9±1.0

Table VI. Szilard-Chalmers effect in NaH_2PO_4

Chemical forms of ^{32}P	Time elapsed after irradiation (days)			
	1	7	8	10
	%	%	%	%
Phosphate	21.2±0.8	28.6±1.0	23.4±0.8	27.1±1.0
Phosphite (+hypophosphite)	17.3±0.3	14.9±0.2	18.8±0.3	15.7±0.3
Pyrophosphate	25.9±5.5	20.7±4.4	25.2±5.4	24.6±5.3
Higher polyphosphates R_f 0.09	19.1±3.2	35.9±0.6	32.4±0.5	31.7±5.5
Higher polyphosphates Others	15.8±8.2			

Table VII. Szilard-Chalmers effect in $(NH_4)_2HPO_4$

Chemical forms of ^{32}P	Time elapsed after irradiation (days)		
	5	7	17
	%	%	%
Phosphate	34.2±1.0	35.3±1.1	36.4±1.2
Phosphite (+hypophosphite)	22.6±0.3	25.1±0.4	23.8±0.4
Pyrophosphate	13.3±4.2	16.0±5.1	15.0±4.8
Higher polyphosphates	24.8±5.3	14.3±3.0	15.3±3.3

Table VIII. Szilard-Chalmers effect in $Na_2HPO_4 \cdot 12H_2O$

Chemical forms of ^{32}P	Time elapsed after irradiation (days)		
	4	7	9
	%	%	%
Phosphate	70.3±1.2	77.8±1.3	84.3±1.4
Phosphite (+hypophosphite)	—	—	—
Pyrophosphate	28.1±0.7	22.2±0.6	15.6±0.4
Higher polyphosphate	1.5±0.2	—	—

Table IX. Szilard-Chalmers effect in Na_2HPO_4

Chemical forms of ^{32}P	Time elapsed after irradiation (day)						
	1	2	3	7	8	9	10
	%	%	%	%	%	%	%
Phosphate	24.3±1.7	22.4±1.5	19.8±1.4	22.0±1.5	25.1±1.7	28.1±1.9	21.7±1.5
Phosphite (+hypophosphite)	20.2±0.4	20.7±0.4	24.3±0.5	21.7±0.4	21.3±0.4	21.2±0.4	23.7±0.5
Pyrophosphate	16.5±2.0	23.8±2.8	19.4±2.3	22.5±2.7	22.4±2.7	19.1±2.3	23.5±2.8
Higher polyphosphates	37.5±2.6	31.5±2.1	34.6±2.4	32.4±2.2	31.0±2.1	31.1±2.1	29.6±2.0

Table X. Szilard-Chalmers effect in $Na_3PO_4 \cdot 12H_2O$

Chemical forms of ^{32}P	Time elapsed after irradiation (days)				
	1	2	5	8	12
	%	%	%	%	%
Phosphate	45.8±1.1	45.2±1.1	53.4±1.3	58.8±1.5	57.6±1.4
Phosphite (+hypophosphite)	47.3±1.2	44.6±1.1	37.2±0.9	30.9±0.8	32.2±0.8
Pyrophosphate Higher polyphosphates	6.7±0.4	10.0±0.7	9.3±0.6	9.8±0.6	9.8±0.6

were not completely separated. Phosphate and phosphite fractions did not show remarkable change with standing time.

Ammonium Dihydrogen Phosphate. — Two samples were tested. Sample I was irradiated in Hole No. 16 (neutron flux: 0.51×10^{12}n/cm^2/sec.) for 1 hr. and Sample II was irradiated, in Hole No. 12 (neutron flux: 0.38×10^{12}n/cm^2/sec.) for 15 hr. The results are shown in Table III. The sum of the fractions of phosphate and phosphite in Table III is almost constant, 61~62%, and the sum of pyrophosphate and higher polyphosphates is 37~38% except for the result after 17 days for Sample II.

Sodium Dihydrogen Phosphates. — Hydrous and anhydrous salts were tested. The results were markedly different from each other.

i) $NaH_2PO_4 \cdot 2H_2O$.—The target was irradiated in the Hole No. 12 (neutron flux: 0.38 10^{12}n/cm^2/sec.) for 15 hr. The results are tabulated in Table IV. The data show some irregularities especially in the fractions of pyrophosphate and higher polyphosphates, but time dependency of the distribution seems to be small. The experiment was not done immediately after irradiation because of the formation of ^{24}Na (half-life: 15.0 hr.).

ii) $NaH_2PO_4 \cdot H_2O$.—The target was irradiated in Hole No. 15 (neutron flux: 0.22×10^{12}n/cm^2/sec.) for 15 hr. The result shown in Table V are similar to those for $NaH_2PO_4 \cdot 2H_2O$.

iii) NaH_2PO_4.—The anhydrous salt was irradiated in Hole No. 3 (neutron flux: 0.48×10^{12} n/cm^2/sec.) for 5 hr. The results shown in Table VI are different from those for the hydrous salts. The difference is as follows. 1) The retention for the anhydrous salt is smaller than those for the hydrous salts. 2) The sum of the pyrophosphate and higher polyphosphate fractions for the anhydrous salt is larger than those for the hydrous salts. 3) The phosphite fraction for the anhydrous salt is larger than that for the hydrous salts.

Diammonium Hydrogen Phosphate.—The target was irradiated in Hole No. 12 (neutron flux: 0.38×10^{12}n/cm^2/sec.) for 15 hr. The results are shown in Table VII.

The sum does not attain to 100% because of the presence of tailing between the spots of pyro- and orthophosphate. The time dependency of distribution seems to be small. Three peaks appear in the fractions of polyphosphates.

Disodium Hydrogen Phosphates. — Both hydrous and anhydrous salts were tested.

i) $Na_2HPO_4 \cdot 12H_2O$.—The target was irradiated in Hole No. 3 (neutron flux: 0.48×10^{12}n/cm^2/sec.) for 5 hr. The results shown in Table VIII are different from the data for $Na_2HPO_4 \cdot 2H_2O$ and $Na_2HPO_4 \cdot 5H_2O$ in Aten's experiments[5]. Phosphite or hypophosphite can not be detected in Table VIII, while a large percentage of phosphite (or hypophosphite) appeared for $Na_2HPO_4 \cdot 2H_2O$ and $Na_2HPO_4 \cdot 5H_2O$ in Aten's work. In the table, the percentage of phosphate slowly increases with standing time while the percentage of pyrophosphate slowly decreases. Apparently, this is likely to be hydrolysis of pyrophosphate in to phosphate.

ii) Na_2HPO_4.—The target was irradiated in Hole No. 3 (neutron flux: 0.48×10^{12}n/cm^2/sec.) for 5 hr. The results are listed in Table IX. These are somewhat different from those in Aten's[5] and Sellers's work[6].

The distribution shows similar tendencies as those for NaH_2PO_4 (Table VI). These results are markedly different from those for the hydrous salt. 1) The retention for the anhydrous salt is smaller than that for the hydrous salt. 2) Fraction of pyrophosphate and higher polyphosphates in the anhydrous salt is larger than that in the hydrous salt. 3) An appreciable fraction of phosphite appears in the anhydrous salt, while it does not appear in the hydrous salts.

Trisodium Phosphates.—Both hydrous and anhydrous salts were tested.

i) $Na_3PO_4 \cdot 12H_2O$.—The target was irradiated in Hole No. 3 (neutron flux: 0.48×10^{12}n/cm^2/sec.) for 5 hr. The results are listed in Table X.

Fractions of phosphate and phosphite show remarkable changes with standing time. In Fig. 2, these changes are shown. Phosphite is slowly converted into phosphate.

ii) Na_3PO_4.—The target was irradiated in Hole No. 3 (neutron flux: 0.48×10^{12}n/cm^2/sec.) for 5 hr. The results are shown in Table XI.

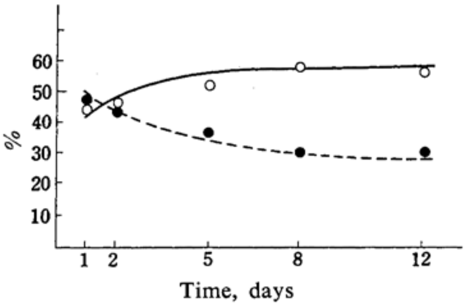

Fig. 2. Variation of percentages of ^{32}P components in $Na_3PO_4 \cdot 12H_2O$. (The phosphate content in % is shown by the solid line and the phosphite (+hypophosphite) content in % is shown by the broken line).

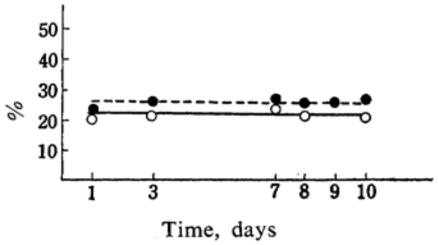

Fig. 3. Variation of percentages of ^{32}P components in Na_3PO_4. (The phosphate content in % is shown by solid line and the phosphite (+hypophosphite) content in shown by the broken line).

Changes of fractions of phosphate and phosphate are shown in Fig. 3. The difference between the results of the hydrous and of the anhydrous salts is as follows. 1) Time dependency is remarkable in the hydrous salt, while it is scarcely ever observed in the anhydrous salt. 2) Retention in the hydrous salt is greater than that in the anhydrous salt. 3) Fractions of pyrophosphate and higher polyphosphates for the anhydrous salts are larger than that those in the hydrous salt.

Zinc Phosphate.—The target was irradiated in Hole No. 3 (neutron flux: 0.48×10^{12}n/cm^2/sec.) for 5 hr. The results are shown in Table XII. The results were similar to those for Na_3PO_4 (anhydrous).

Sodium Phosphite ($Na_2HPO_3 \cdot 5H_2O$). — The target was irradiated in Hole No. 3 (neutron flux: 0.48×10^{12}n/cm^2/sec.) for 5 hr. The results are tabulated in Table XIII.

TABLE XI. SZILARD-CHALMER EFFECT IN Na_3PO_4

Chemical forms of ^{32}P	Time elapsed after irradiation (days)					
	1	3	7	8	9	10
	%	%	%	%	%	%
Phosphate	20.7±0.5	22.1±0.6	23.5±0.6	22.2±0.6	25.9±0.7	28.4±0.7
Phosphite (+hypo-phosphite	24.2±0.6	26.3±0.6	27.3±0.6	25.9±0.6	25.7±0.6	23.2±0.6
Pyrophosphate	18.3±5.0	47.0±1.0	48.2±1.0	16.8±4.8	18.2±5.0	19.4±5.2
Higher polyphosphates	35.1±7.7			32.2±7.0	28.8±6.3	28.4±6.2

Table XII. Szilard-Chalmers effect in $Zn_3(PO_4)_2$

Chemical forms of ^{32}P	Time elapsed after irradiation (days)	
	1	7
	%	%
Phosphate	29.6±1.1	34.5±1.3
Phophate (hypophosphite)	36.2±1.4	35.7±1.2
Pyrophosphite	9.3±0.9	28.8±0.6
Higher polyphosphates	24.8±2.0	

Table XIII. Szilard-Chalmers effect in $Na_2HPO_3\cdot 5H_2O$

Chemical forms of ^{32}P	Time elapsed after irradiation (days)			
	2	5	12	15
	%	%	%	%
Phosphate	4.5±0.1	4.3±0.1	4.0±0.1	2.9±0.1
Phosphite (+hypophosphite)	77.2±8.3	76.0±8.2	77.9±8.4	82.0±8.9
Pyrophosphate	9.6±0.9	7.6±0.7	5.4±0.5	4.8±0.5
Higher polyphosphates	7.6±0.7	10.9±1.0	7.6±0.7	7.5±0.7

Table XIV. Szilard-Chalmers effect in $Na_4P_2O_7\cdot 10H_2O$

Chemical forms of ^{32}P	Time elapsed after irradiation (days)				
	2	5	12	15	22
	%	%	%	%	%
Phosphate	47.9±2.4	44.2±2.2	51.4±2.5	53.9±2.7	50.2±2.5
Phosphite (+hypophosphite)	—	—	—	—	—
Pyrophosphate	45.3±2.3	43.4±2.2	35.5±1.8	34.5±1.8	38.1±1.9
Higher polyposphates	7.1±0.5	12.1±0.9	12.8±0.9	11.0±0.8	11.6±0.8

Table XV. Szilard-Chalmers effect in $Na_4P_2O_7$

Chemical forms of ^{32}P	Time elapsed after irradiation (days)
	4
	%
Phosphate	9.4±1.6
Phosphite (+hypophosphite)	24.8±0.9
Pyrophosphate	36.2±4.2
Higher polyphosphates	26.5±2.3

Several components also appear in the chromatogram, but the major component is the parent substance. Pyrophosphate and higher polyphosphates are detected in appreciable quantities. Changes by standing time are not great.

Sodium Pyrophosphates.—Both hydrous and anhydrous salts were tested.

i) *$Na_4P_2O_7\cdot 10H_2O$*.—The target was irradiated in Hole No. 3 (neutron flux: 0.48×10^{12} n/cm²/sec.) for 5 hr. The results are listed in Table XIV.

The distribution slightly changed by standing time.

ii) *$Na_4P_2O_7$*.—The anhydrous salt was irradiated in Hole No. 12 (neutron flux: 0.38×10^{12} n/cm²/sec.) for 15 hr. The result is shown in Table XV.

There are great differences between the results of the hydrous and of the anhydrous salt. 1) The phosphate fraction in the anhydrous salt is much smaller than that in the hydrous salt. 2) The phosphite fraction is not detected for the hydrous salt, while it is more than 20% for the anhydrous salt.

Discussion

On the study on the Szilard-Chalmers effect, the exchange reaction between the separated atoms and parent substance is an important factor. If this exchange reaction occurred rapidly, we could not observe the Szilard-Chalmers effect. Several exchange reactions of phosphorus acids have been investigated so far. No isotopic exchange of phosphorus was detected in the systems: $H_3PO_4+H_3PO_2$[9,10], $H_3PO_4+H_3PO_3$[10,11], $H_3PO_4+(HPO_3)_3$[12], $(NaPO_3)_3+(NaPO_3)_6$ and $(NaPO_3)_3$[13], $NaH_2PO_4+(NaPO_3)_6$[13]. Therefore, the effect of the exchange reaction between the parent substance and the daughter species can be ignored in the present paper. The phosphite fraction seems to become larger in the order of the targets of phosphoric acid, primary, secondary and tertiary phosphate. But this is not applicable to the hydrous salts.

Ammonium chromate[14] and iodate[15] show a much lower retention value in the Szilard-Chalmers effect than other alkali chromates and iodates do. Namely, the yield of the reduced form for the ammonium salts is much higher than that for other alkali salts. Therefore, Harbottle et al.[16] suggested that the ammonium ion may act as a reducing agent in the hot zone. However, in the present case the yield of the reduced forms for ammonium phosphates is not markedly higher than that for the corresponding alkali phosphates. Perhaps the ammonium ion does not act as a reducing agent to phosphate in the hot zone. This may be attributed to the difference in oxidation potential of phosphate and chromate or iodate to their reduced forms.

Remarkable differences are present between the Szilard-Chalmers effects of anhydrous and hydrous phosphates. Retention in the Szilard-Chalmers effect of the hydrous salt is generally greater than that of the anhydrous salt. In the cases of $NaH_2PO_4\cdot 2H_2O$, $NaH_2PO_4\cdot H_2O$ and $Na_2HPO_4\cdot 12H_2O$, the fraction of phosphite (or hypophosphite) is smaller than that in the anhydrous salts. Similar effects are observed in the cases of hydrous and anhydrous sodium pyrophosphates. The water molecule seems to act as an oxidizing agent for these salts. However, in the case of $Na_3PO_4\cdot 12H_2O$, the fraction of phosphite (+hypophosphite) is larger than that for the anhydrous salt. This seems to be inconsistent with the fact that the water molecule apparently acts as an oxidizing agent in the former cases, but the reason is not yet clear. Usually phosphite (or hypophosphite) changes slowly into phosphate by standing in the case of the hydrous salt, while it scarcely changes in the case of the anhydrous salt. This time dependency may be attributable to the formation of any oxidizing agent in the presence of the water molecule. Phosphite (or hypophoshite) may react slowly with this oxidizing agent and change into phosphate. Fractions of pyrophosphate and higher polyphosphates are smaller for the hydrous salt than those of the anhydrous salt. This fact may be interpreted by the dilution effect (or any other hindrance effect) of the water molecule on the condensation of phosphate in the solid state.

Formation of pyrophosphate and higher polyphosphates occurs in all phosphorus acids and their salts which have been tested. The presence of higher polyphosphates has not been pointed out clear by so far. The condensation reaction of phosphate to condensed polyphosphates usually occurs at a high temperature. For example, orthophosphoric acid is converted into pyrophosphoric acid by heating at 250°C. Therefore, the experiments may suggest that the high temperature reactions play important roles in the present cases. Really, at the event of the recoil a large amount of heat is liberated, and it is expected that the neighbor of the recoil atom is raised up to a high temperature[17]. According to the calculation based on the theory of Hatbottle et al.[17], the hot zone in an ionic crystal includes about 1000 atoms at 1000°K, and about 2000 atoms at 500°K, provided that the recoil energy is about 300 eV.

The spot at the R_f value of 0.09 appears only in the primary phosphates. This is likely to correspond to polymetaphosphate. This may be produced by the following reaction:

$$n\mathrm{MH_2PO_4} \rightarrow (\mathrm{MPO_3})_n + n\mathrm{H_2O}.$$

In the cases of the molecular and ionic crystals which are unstable to heat, the mechanism of the thermal reaction in the hot-zone is likely to be very important. This localized thermal reaction or high temperature reaction may be necessary to explain some complicated phenomena in the Szilard-Chalmers effect.

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