The Thermal Annealing of Phosphorus-32 Formed by the Neutron Irradiation of Several Inorganic Phosphorus Compounds

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(Received April 6, 1963)

The distribution of chemical forms of phosphorus-32 in neutron-irradiated phosphorus compounds has been reported on by several investigators[1-8]. It has been found that these phenomena are very complicated. It seems important to solve the problem that the proportions of the different chemical species of phosphorus-32 appear to depend on various complicated factors: the effect of thermal annealing, which has proceeded during and after the neutron irradiation, the chemical form of the target materials[9], and the circumstances during neutron irradiation[10]. The change in the distribution of phosphorus-32 in various chemical forms after neutron irradiation of phosphorus compounds has been pointed out by Lindner and Harbottle[11] and also by Yoshihara and Yokoshima[12]. They treated the

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[4] I. G. A. Fiskell, W. A. Delong and W. F. Oliver, *Can. J. Chem.*, **30**, 9 (1952).

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

[6] T. R. Sato, P. A. Sellors and H. H. Strain, ibid., **7**, 84 (1959).

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[10] T. R. Sato and H. H. Strain, "Proceedings of the Symposium on Chemical Effects of Nuclear Transformations", Vol. I, I A E A, Prague (1961), p. 503.

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[12] K. Yoshihara and T. Yokoshima, This Bulletin, **34**, 123 (1961).

irradiated salts at room temperature and suggested a specific interpretation of the change in the proportion of the distributed chemical species. Claridge and Maddock[13] have performed thermal annealing experiments using the precipitation method for the separation of chemical species and have suggested an increase in retention and in the threshold temperature as the result of thermal annealing.

Green and Maddock[14] first found that the retention in the Szilard-Chalmers process was increased by the thermal annealing of heating-irradiated chromates. The activation energy for this process has been shown by Harbottle and Sutin[15] to be the energy of the recombination reaction of fragments formed by recoil phenomena. In their treatment for thermal annealing, the term of the change of the retention meant the composite process of change in all the species chemically distributed. In the case of phosphorus recoil chemistry, however, such a treatment of " retention " may give somewhat ambiguous results in the analysis of the given annealing curves.

In a previous communication[16] the present authors pointed out the different behaviour of the different fractions of phosphorus-32 upon thermal annealing. It should be considered that the activation energy of the thermal annealing process of each fraction differs from that of the retention.

In this paper, the authors will describe a detailed study of the thermal-annealing effect of phosphorus-32 in the distributed chemical species with several anhydrous inorganic phosphates and pyrophosphate in crystal, and will report their findings on the activation energies of separated fractions of phosphorus-32.

Experimental

Target Materials.—The sodium dihydrogen phosphate and sodium dihydrogen phosphite used were guaranteed reagents of the Wako Chemicals Co. while the disodium hydrogen phosphate, potassium dihydrogen phosphate, sodium pyrophosphate, and disodium hydrogen phosphite were guaranteed reagents of the Kanto Chemicals Co. Each of these hydrated salts, except potassium dihydrogen phosphate and sodium pyrophosphate, was dehydrated upon heating in a porcelain dish, and evaporating it to near dryness. All salts were dried in vacuo at 100°C for one night over phosphorus pentoxide. Anhydrous trisodium phosphate was prepared from $Na_3PO_4 \cdot 12H_2O$ in the same way. The content of sodium or potassium ions in these salts was determined by flame photometry using a Perkin-Elmer flame photomater. The purity of anions was tested by activation analysis as follows: a small portion of each salt was dissolved in water and was subjected to paper chromatographic separation. Dried paper strips were irradiated in a nuclear reactor, and were cut to pieces 1 cm. in width. The radioactivity was counted by a GM counter 2 weeks after the end of the neutron irradiation. The purity was calculated from the percentage of the radioactivity of the fraction at the corresponding position on the strips. The results are tabulated in Table I.

TABLE I. PURITY OF TARGET MATERIALS

Target material	Anionic %	Cationic* %
NaH_2PO_4	96	99
Na_2HPO_4	99	99
Na_3PO_4	99	60
$Na_4P_2O_7$	88	99
Na_2HPO_3	98	—
KH_2PO_4	94	—

* Purity as corresponding molecular form.

Neutron Irradiation.—The irradiations were mainly performed in the irradiation hole No. 12 (a vertical hole; thermal neutron flux 4.8×10^{11} n/cm^2·sec.) of JRR-1 (a water boiler reactor operated at 40 kW) for 15 hr. The salts which had been sealed in polyethylene tube in the presence of air were placed in an ambient reactor temperature. After being stored for 1 week at room temperature, the salts were subjected to thermal-annealing experiments. For irradiation and storage, all of the salts were maintained in as constant a condition as possible in order to avoid a change in the initial distribution of phosphorus-32 species.

Thermal-Annealing and Chemical Separation.—The irradiated salts were heated in a quartz boat (size: $10.5 \times 1.2 \times 1.2$ cm^3) which was placed in a thermostatically-controlled electric furnace (a quartz cylinder 2.4 cm. in diameter was used for heating the samples). The samples were inserted at the center of the cylinder, and a Pt-Rh thermostat was operated at the same time. A small portion of the heated samples in the boat was taken into the small water-cooled glass bottle at definite time intervals and was dissolved in a sufficient volume of water.

The separation and identification of the chemical species of phosphorus-32 were accomplished by paper chromatography. Two methods were tried for separation. One of them was that reported previously by one of the present authors, using the Toyoroshi No. 53 (2 cm.×40 cm.) to separate the polyphosphates and orthophosphate fractions. One drop of the sample solution was put on filter paper (5 cm. from the end of the strip), dried in air, and developed by the one-dimensional ascending method with 2 N nitric acid-saturated *n*-butanol for about 24 hr. Another method was chosen to separate the fraction in such reduced species as phosphite and

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[13] R. F. C. Claridge and A. G. Maddock, " Proceedings of the Symposium on Chemical Effects of Nuclear Transformations ", Vol. I, I A E A, Prague (1961), p. 475.

[14] I. H. Green and A. G. Maddock, *Nature*, **164**, 788 (1949).

[15] G. Harbottle and N. Sutin, " Advances in Inorganic Chemistry and Radiochemistry ", Vol. 1. Ed., by H. J. Emeleus and A. G. Sharpe, Academic Press, New York and London. (1959), p. 305.

[16] H. Baba, K. Yoshihara, H. Amano, K. Tanaka and N. Shibata, This Bulletin **34**, 590 (1961).

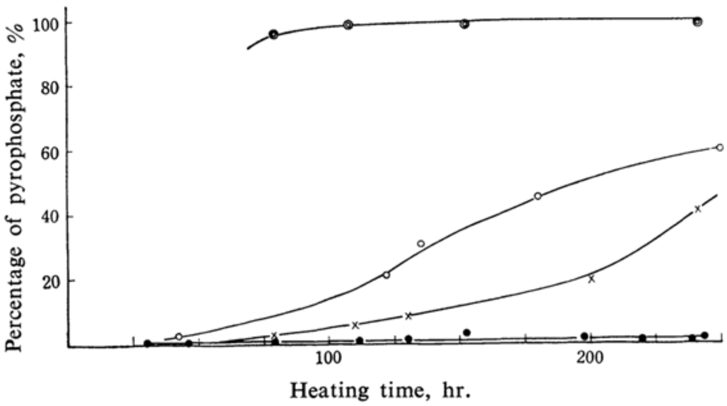

Fig. 1. Formation of pyrophosphate by heating several phosphates.
—×— Sodium dihydrogen phosphate at 150°C
—◎— Sodium dihydrogen phosphate at 200°C
—●— Disodium hydrogen phosphate at 150°C
—○— Disodium hydrogen phosphate at 200°C
For trisodium phosphate, sodium pyrophosphate and disodium hydrogen phosphite no change of chemical species is observed by heating at 200°C for 230 hr.

hypophosphite from the bulk of the neutron-irradiated salts. Pretreated filter paper was used in this case; the paper was preliminarily immersed into a solution of dilute hydrochloric acid for 1 day, soaked with redistilled water for another day, washed repeatedly with water, and dried in air; it was then developed with a mixture of 1 N ammonia, dioxane, and *n*-butanol (1 : 1 : 1 volume ratio) for 20 hr.

Counting Procedure.—After developing and drying, the paper was cut into pieces 1 cm. in width. The radioactivity of the pieces was measured by a thin end window-type GM gas flow counter at a constant geometry. Decay curves were drawn for all salts. Counting was started at least 10 days after the end of neutron irradiation in order to avoid errors besed on the radioactivity of sodium-24 or potassium-42. The gamma ray spectra of salts were measured with a NaI scintillation spectrometer in order to verify the absence of other activities.

A Test of the Pyrolysis of the Target Materials.—The target materials, which had not been neutron-irradiated, were heated under the same conditions as in the thermal-annealing experiments but for a comparatively prolonged time. The heated samples were dissolved in water, and the anions were separated by paper chromatography with 2 N nitric acid-saturated *n*-butanol. The strip of paper was dried in air and was subjected to neutron irradiation in a reactor. The radioactivity on the paper was counted with a GM counter 2 weeks after the end of neutron irradiation, and the percentage of the fraction of polyphosphate was estimated. Figure 1 shows the pyrophosphate formed by heating sodium dihydrogen phosphate and disodium hydrogen phosphate at 150∼200°C versus the heating time. The formation of neither such higher polyphosphates as tripolyphosphate, tetrapolyphosphate and Grahams' salt, nor such reduction products as phosphite and hypophosphite was detected in any of the salts used here.

Results and Discussion

Figures 2 and 3 are histograms of paper chromatography showing the distribution of phosphorus-32 in various chemical species. The results obtained by development with nitric acid-saturated *n*-butanol are shown in Fig. 2, while those obtained by development with the mixture of 1 N ammonia, dioxane and *n*-butanol are shown in Fig. 3. The several peaks found in the histograms are noted as A, B, C, etc.

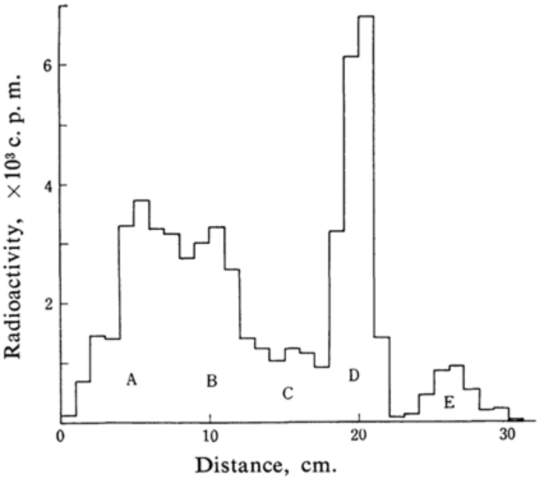

Fig. 2. Chromatographic separation of neutron irradiated disodium hydrogen phosphate with 2 N nitric acid saturated *n*-butanol.

From the R_f value in the chromatograms, it is indicated that the A and B fractions corresponded to the mixture of such higher polyphosphates as tripolyphosphate and polymerized metaphosphates. Pyrophosphate was found in C fractions and orthophosphate, in D fractions. A mixture of phosphite and hypophosphite appeared in E fractions. The separation among A, B and C fractions was not very significant, so the sum of A, B and C was identified as a polyphosphate fraction. In the case of pyrophosphate salt, the sum of the A and B fractions was denoted as a polyphosphate fraction. The E fraction was noted as a reduced species fraction, and D, as an orthophosphate fraction. These assignments were also expected from the results of other experiment(17). The percentage of the F fraction is equal to the sum of A, B, C and D, the percentage of the E fraction also corresponds to the sum of G and H, while the G fraction can not be identified as phosphite because a low R_f value of the G fraction compared with that of phosphite is obtained. The R_f value of the H fraction is in agreement with that of hypophosphite.

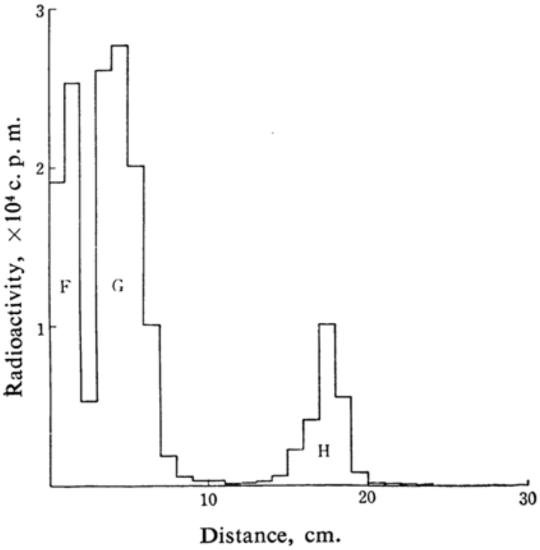

Fig. 3. Chromatographic separation of neutron irradiated disodium hydrogen phosphite with mixed solution (1 : 1 : 1) of 1 N ammonia, dioxane and *n*-butanol.

The samples irradiated in a nuclear reactor were heated in the temperature range of 85～200°C. Similar annealing curves were obtained from all of the orthophosphate salts used. Typical examples of these annealing against the logarithm of time are shown in Figs. 4, 5 and 6. The proportion of phosphorus-32 in the fraction is registered on the ordinate, while on the absissa the heating time is given in minutes. The percentage of the activities in the polyphosphate fraction decreases remarkably, while only a slight decrease is observed in the case of the reduced-species fractions. However, retention as orthophosphate always increases. The annealing curves given from sodium pyrophosphate are very similar to that of orthophosphate salts, but the orthophosphate fraction is a little changed. In the case of sodium phosphite, quite different annealing behavior is observed. Retention as the phosphite fraction increases while an increase in the hypophosphite fraction occurs at the same

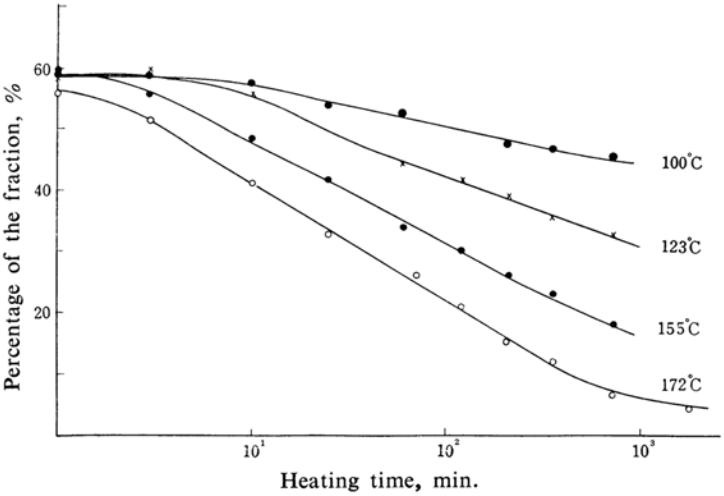

Fig. 4. Isothermal annealing curves for the polyphosphate fraction in irradiated disodium hydrogen phosphate.

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17) K. Tanaka, to be published.

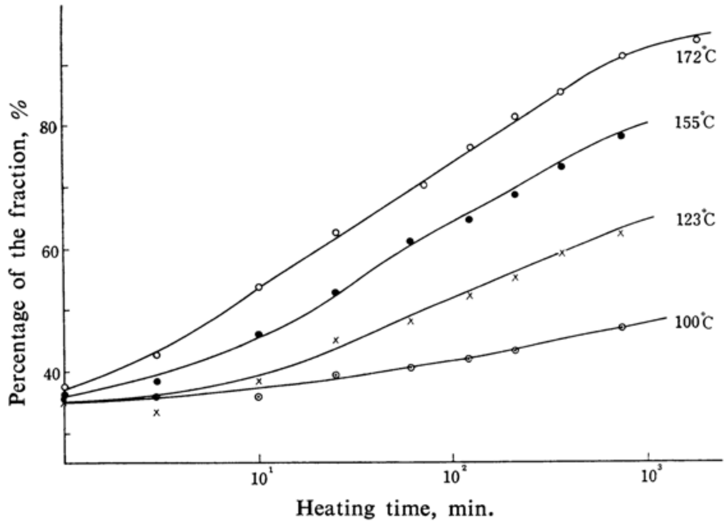

Fig. 5. Isothermal annealing curves for the retention as orthophosphate in irradiated disodium hydrogen phosphate.

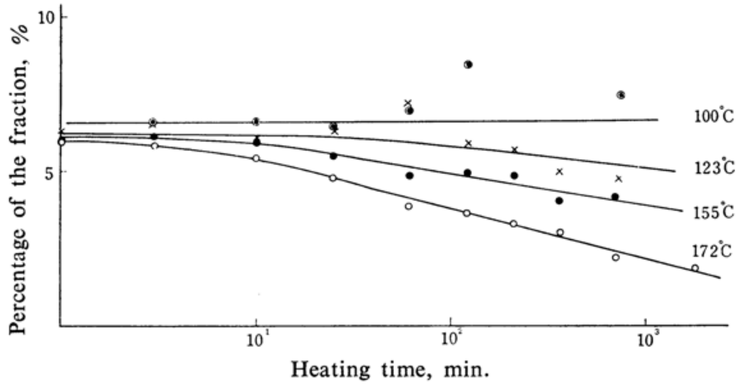

Fig. 6. Isothermal annealing curves for the reduced species fraction in irradiated disodium hydrogen phosphate.

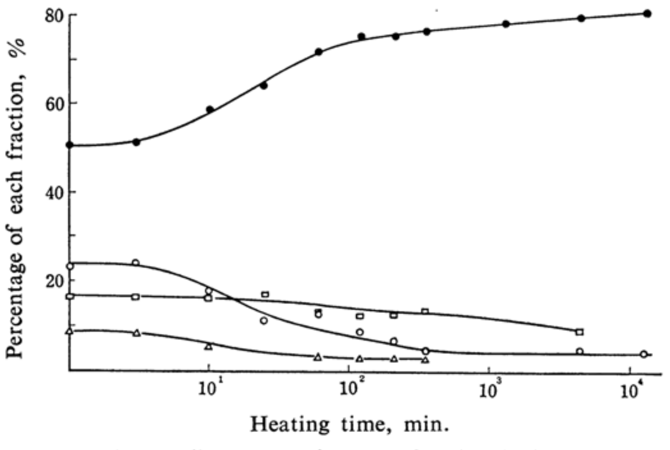

Fig. 7. Isothermal annealing curves for each fraction in irradiated sodium pyrophosphate at 200°C.

—○— The polyphosphate fraction —●— The pyrophosphate fraction (retention)
—△— The orthophosphate fraction —□— The reduced species fraction

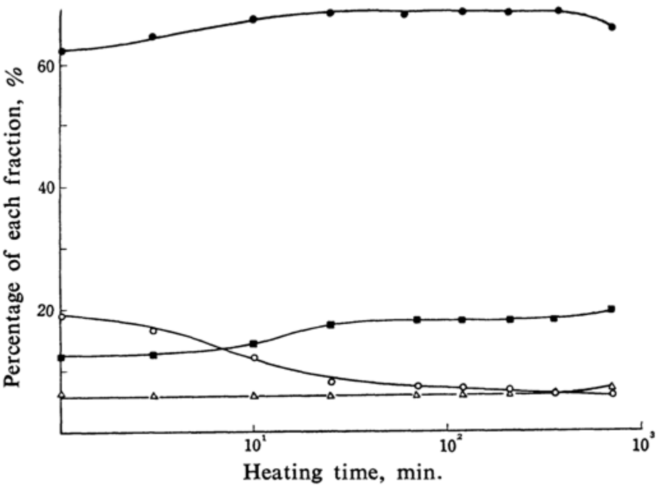

Fig. 8. Isothermal annealing curves for each fraction in irradiated disodium hydrogen phosphite at 172°C.

—○— The polyphosphate fraction	—△— The orthophosphate fraction
—●— The phosphite fraction (retention)	—■— The hypophosphite fraction

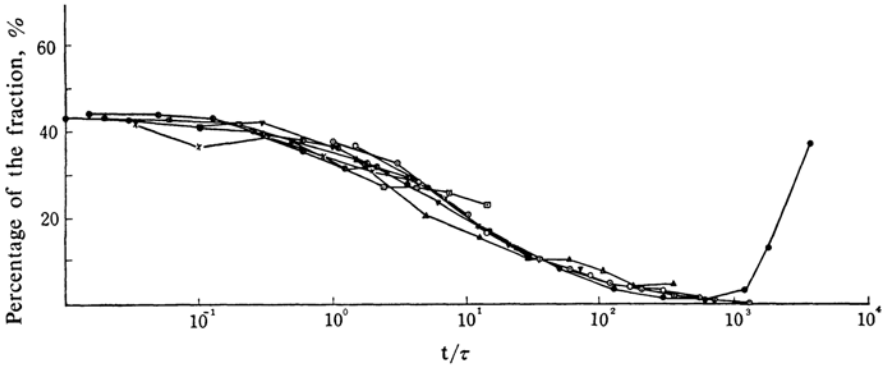

Fig. 9. Composite annealing curves for superposition with respect to the polyphosphate fraction in irradiated potassium dihydrogen phosphate at 165°C.

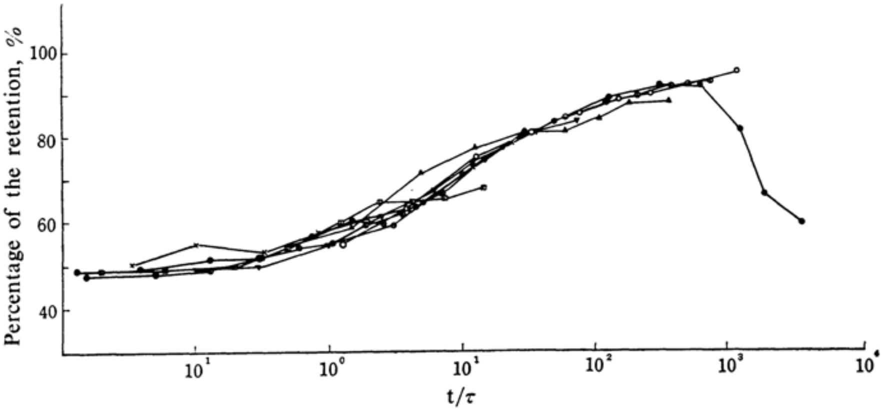

Fig. 10. Composite annealing curves for superposition with respect to the orthophosphate fraction (retention) in irradiated potassium dihydrogen phosphate at 165°C.

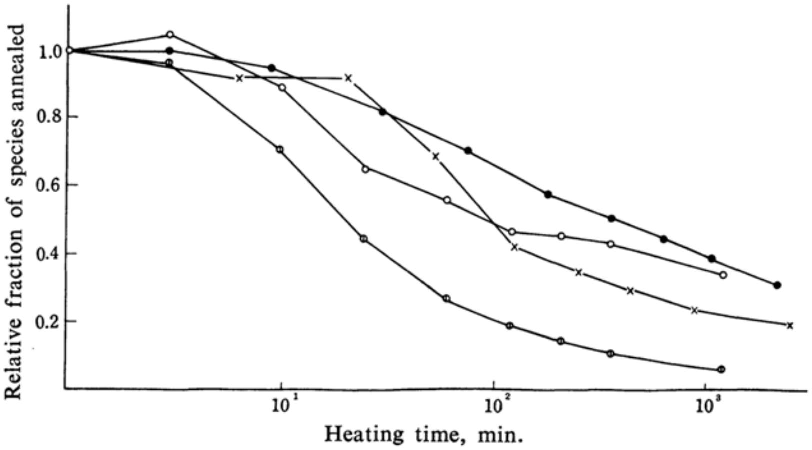

Fig. 11. Isothermal annealing curves for the polyphosphate fraction in irradiated certain phosphates at 140°C.

—○— Sodium dihydrogen phosphate —●— Disodium hydrogen phosphate
—×— Trisodium phosphate —⦶— Potassium dihydrogen phosphate

time, and only a decrease in the polyphosphate fraction is shown. The composition of the polyphosphate fraction may differ from that of the polyphosphate fraction in phosphate crystals. The results obtained from each of the irradiated salts are shown in Figs. 7 and 8.

For thermal annealing in every salt used here except sodium dihydrogen phosphite, the amount of the increase in retention corresponded to the sum of the decrease in the other fractions. From the results with orthophosphate and pyrophosphate salts, it is found that there is some difference in the annealing behavior between polyphosphate and reduced species. At the initial step, the majority of annealing reaction consists of the reaction of the polyphosphates fraction. This is also found in the case of the phosphite sample. The annealing effect of the reduced species fraction gradually becomes more predominant on prolonged heating.

Fletcher and Brown[18] assumed that the thermal annealing was represented by an expression in which t/τ was the ultimate variable. In this case τ was arbitrarily chosen. In order to obtain a composite annealing curve, the temperature interval was pursued more precisely that of the above experiments. In this treatment we found, that these curves showed the temperature dependency of the annealing behavior. An equivalent annealing curve for 165°C for potassium dihydrogen phosphate is shown in Figs. 9 and 10. These curves show that there might be little difference in the annealing kinetics in this temperature range since a good overlapping of all the curves is to be seen here. The curves given from the change in the proportions of the polyphosphate fraction are each compared with some of different orthophosphate samples in

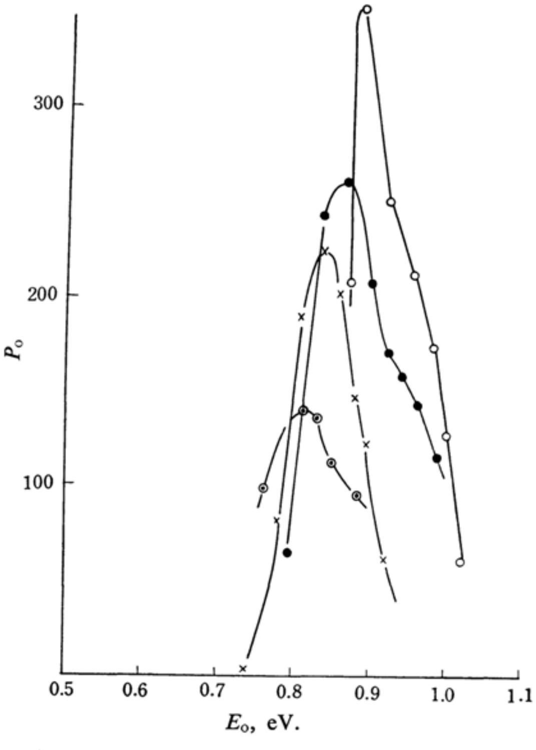

Fig. 12. The initial distribution of activation energy for the polyphosphate fraction in irradiated sodium dihydrogen phosphate.

—⊙— at 90°C —×— at 112°C
—●— at 140°C —○— at 166°C

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[18] R. C. Fletcher and W. L. Brown, *Phys. Rev.*, **92**, 585, 591 (1953),

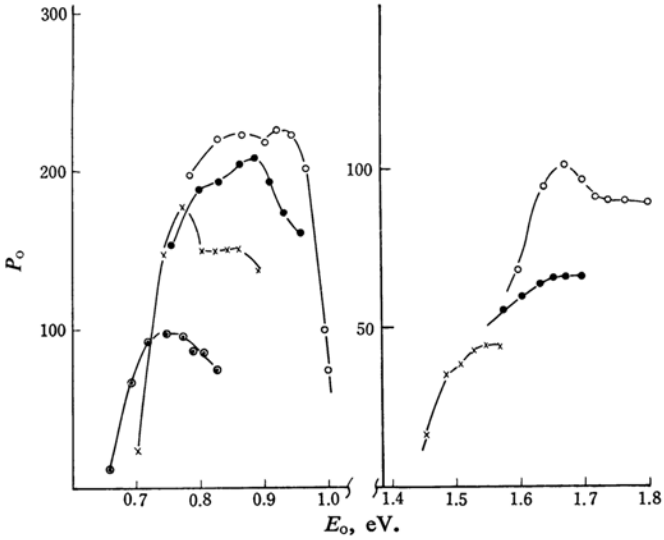

Fig. 13. The initial distribution of activation energy for ^{32}P in irradiated disodium hydrogen phosphate.
Left hand side——the polyphosphate fraction
Right hand side——the reduced species fraction.
—⊙— at 100°C —×— at 123°C —●— at 155°C —○— at 172°C

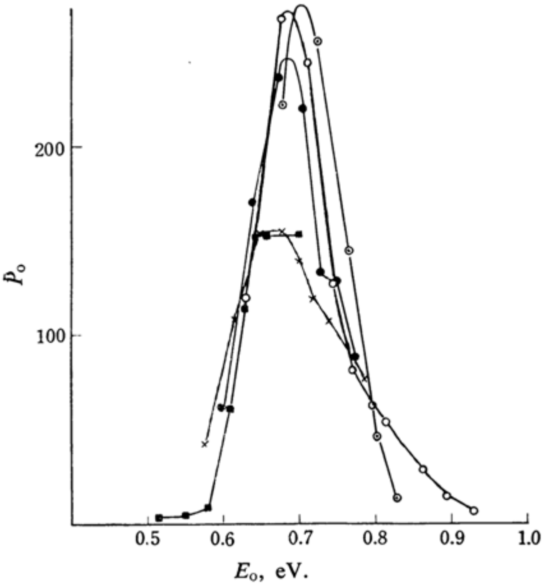

Fig. 14. The initial distribution of activation energy for the polyphosphate fraction in irradiated trisodium phosphate.
—■— at 85°C —×— at 127°C
—●— at 144°C —○— at 167°C
—⊙— at 200°C

Fig. 11. On the ordinate the initial proportions of the polyphosphate fraction in irradiated phosphates are plotted as a unity. There are some differences in the annealing curves given from the orthophosphate samples used. However, no definite dependency on the chemical forms of the target materials is found.

It has been found by many investigators that thermal annealing can be described formally by first order kinetics at the initial step of annealing and then followed by second order kinetics. Our results can not accurately be fitted to a definite order of kinetics. For the determination of the activation energy we have adopted Vands' concept[19] as amplified by Primak[20]. If it is assumed that the kinetics can be explained by processes with distributed activation energies, the approximate initial distribution of the activation energy, P_o, for the percentage changes in fractions are given by $(-1/\boldsymbol{k}T)\mathrm{d}p/\mathrm{d}(\ln t)$ vs. $E_o=\boldsymbol{k}T \ln (B_f\, t)$, where E_o is the activation energy in eV., p is the fraction annealed at the time t, B_f is a constant having the dimension of frequency, $\boldsymbol{k}$ is Boltzman's constant, and T is the absolute temperature. This treatment has already been adopted by several authors[15,21,22]. The B_f factor was taken as the best overlapping of successive annealing curves. The estimated values of B_f are described in Table II. The initial distribution of activation energies is plotted in Figs. 12—17. The activation energies of the annealing of the polyphosphate fraction are mostly distributed between 0.60 and 1.0 eV.,

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[19] V. Vand, *Proc. Phys. Soc.*, **55**, 222 (1943).

[20] W. Primak, *Phys. Rev.*, **100**, 1677 (1955).

[21] F. P. Clarke, *Discussions Faraday Soc.*, **23**, 141, 170 (1957).

[22] T. Costea, *J. Inorg. Nucl. Chem.*, **19**, 27 (1961).

TABLE II. ESTIMATED VALUE OF FACTOR B_f

	log B_f		
Irradiated sample	Retention	Fraction as polyphosphate	Fraction in reduced species
NaH_2PO_4	7.4	7.4	Uncertain
Na_2HPO_4	7.2	6.6	11.3
Na_3PO_4	8.3	5.0	Uncertain
$Na_4P_2O_7$	8.4	9.2	Uncertain
Na_2HPO_3	—	5.6	Uncertain
KH_2PO_4	6.6	6.5	10.3

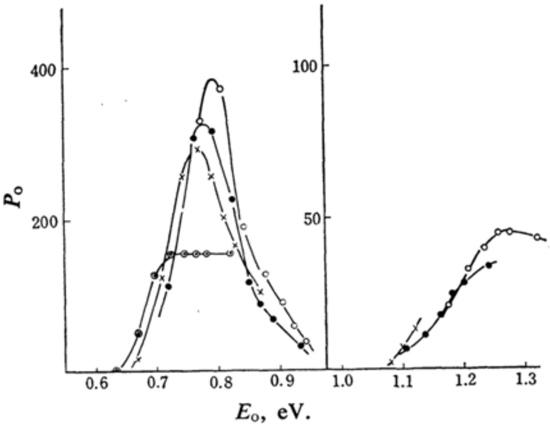

Fig. 15. The initial distribution of activation energy for ^{32}P in irradiated potassium dihydrogen phosphate.
Left hand side——the polyphosphate fraction
Right hand side——the reduced species fraction.
—⊙— at 90°C —×— at 112°C
—●— at 140°C —○— at 166°C

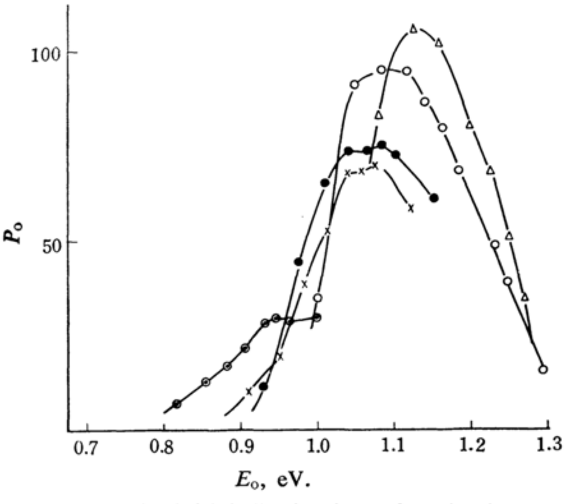

Fig. 16. The initial distribution of activation energy for the polyphosphate fraction in irradiated sodium pyrophosphate.
—⊙— at 85°C —×— at 127°C
—●— at 137°C —○— at 167°C
—△— at 200°C

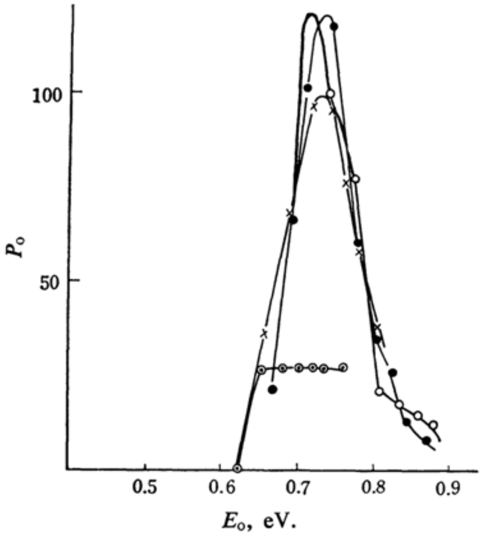

Fig. 17. The initial distribution of activation energy for the polyphosphate fraction in irradiated sodium dihydrogen phosphite.
—⊙— at 100°C —×— at 123°C
—●— at 155°C —○— at 172°C

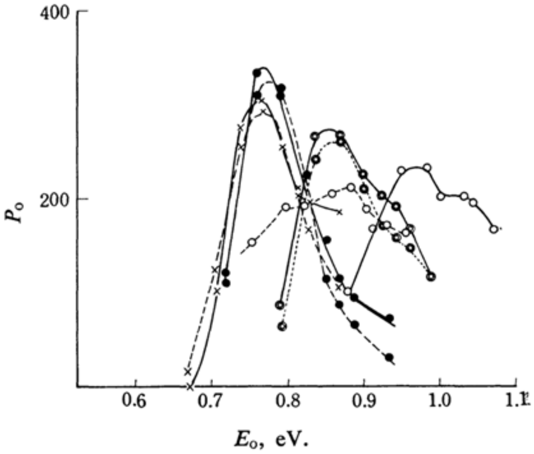

Fig. 18. The initial distribution of activation energy for retention as orthophosphate in irradiated certain phosphates.
---×--- The polyphosphate fraction, at 112°C, KH_2PO_4
---●--- The polyphosphate fraction, at 140°C, KH_2PO_4
—×— Orthophosphate (retention), at 112°C, KH_2PO_4
—●— Orthophosphate, (retention), at 140°C, KH_2PO_4
---◎--- The polyphosphate fraction, at 140°C, NaH_2PO_4
—◎— Orthophosphate (retention), at 140°C, NaH_2PO_4
---○--- The polyphosphate fraction, at 155°C, Na_2HPO_4
—○— Orthophosphate (retention), at 155°C, Na_2HPO_4

except for the pyrophosphate sample, in which the polyphosphate fraction is annealed with the activation energy distributed between 0.78 and 1.3 eV. Much larger errors are found when the B_f factor is obtained from the annealing of the reduced species fraction because the annealing conditions are limited. However, it is clear that the activation energies of these fractions are distributed higher than that of the polyphosphate fraction. These distribution curves are given in Figs. 13 and 15. The distribution curve starts at 1.4 eV. for disodium hydrogen phosphate and 1.1 eV. for potassium dihydrogen phosphate.

In Fig. 19 the distribution of activation energies for the annealing of the polyphosphate fraction is compared with that of retention as orthophosphate in the case of three kinds of orthophosphate samples. It is found that the distribution curves given from the thermal annealing of retention are very similar to those of the polyphosphate fraction. This means that the distribution curve of activation energy given from the thermal annealing in retention shows only the majority of the fractions annealed, so the annealing behavior seems to be quite different from each particular fraction annealed. Therefore, in the annealing of the phosphate samples used it is possible that the results obtained from the thermal annealing of retention indicate a composite of discrete thermal annealing curves. There would be some advantage in separating the species more elaborately.

The proportions of phosphorus-32 in the polyphosphate fraction show an abnormal increase on prolonged heating at 167 and 200°C in the case of the sodium dihydrogen phosphate and disodium hydrogen phosphate samples. This change is attributed to the formation of pyrophosphate by the pyrolysis of salts shown in Fig. 1. This is confirmed by the activation analysis of chromatographically-separated paper strips after the decaying out of phosphorus-32.

Summary

Thermal annealing curves given from the chemically-distributed phosphorus-32 formed by neuton irradiation in a nuclear reactor were obtained by heating several orthophosphates, sodium pyrophosphate, and disodium hydrogen phosphite samples in crystal. The separation was accomplished by one-dimensional paper chromatography. The amounts of phosphorus-32 in the chemical species different from the parent species decreased upon the heating of the salts, except in the case of sodium dihydrogen phosphite, whereas retention always increased.

By the analysis of thermal annealing curves obtained from the initial distribution of activation energies, it was found that there was a difference between the thermal-annealing behavior of the polyphosphate fraction and that of the reduced species fraction. The activation energies of the polyphosphate fractions were in the range of 0.60 to 1.0 eV., but the pyrophosphate sample showed an exceptionally high value, i. e., 0.78 to 1.3 eV. Higher activation energy values were estimated for the annealing of the reduced species fraction than for those of the polyphosphate fractions.

The authors wish to express their deep gratitude to Dr. Kenjiro Kimura, the Director of this Institute, and to Professor Nobufusa Saito of The University of Tokyo, for their guidance and valuable suggestions. Their thanks are also due to Dr. Nagao Shibata and Dr. Hiroshi Amano for their encouragement throughout this work.

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