3450 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(12), 3450—3455 (1975) [Vol. 48, No. 12

Chemical Effects of $^{31}P(n,\gamma)^{32}P$ Reaction in Phosphate Glass—A Radiation Chemical Approach to Hot Atom Chemistry

Tsing-Ko LIN and Niro MATSUURA*

Institute of Nuclear Energy Research, P.O. Box 3, Lung-Tan, Taiwan, Republic of China

**Department of Pure and Applied Sciences, College of General Education, University of Tokyo, Tokyo 153*

(Received March 25, 1975)

Sodium metaphosphate glass, with a polymerization degree of 50—100, was used as target material for the study of the chemical effects of (n, γ) reaction. Mean oxidation number of ^{32}P was introduced as a new parameter to elucidate the oxidation reaction brought on the recoil product. The mean oxidation number of ^{32}P from (n, γ) recoil in such glassy polyphosphate was about +4. More than 90% of the ^{32}P set free was reattached as an end group in the newly formed radioactive polyphosphate. The recoiled monoatomic ^{32}P species (less than 10% of the total ^{32}P) defficient in oxygen kept a low mean oxidation number *ca.* +3. Ionizing radiation produced color center (with λ_{max} at 510 nm) which seemed partially to oxidize the ^{32}P product. The effect was very weak, and could be suppressed by the hold scavengers. Thermal annealing showed that the mean oxidation number of ^{32}P rapidly attained +5 (the valence of target) by 300 °C; however, it seems very difficult to raise the mean oxidation number of ^{32}P to +5 by γ-ray annealing. The oxidation of ^{32}P through thermal annealing is considered to be a diffusion process, with an activation energy of *ca.* 7×10^3 cal/mol. Possible reaction between the hot-zone and the radiation spurs is discussed.

During the course of $^{31}P(n, \gamma)$ ^{32}P reaction in oxyphosphorus compounds, more than 90% of the recoil ^{32}P was set free from its bonding. However, most of the ^{32}P underwent recombination to form radiophosphates even in polymer skeletones.[1] Electrophoretic study of the reactor-irradiated oxyphosphates of ammonium and alkali metal salts at liquid nitrogen temperature indicates that fourteen different anions labelled with ^{32}P in the skeletones of polymer species were found.[2,3] Such ^{32}P-labelled polyphosphates were also observed in the aqueous target of varilous orthophosphate solutions.[4] Our experiments with polyphosphates as target clarified how the recoil ^{32}P was converted into the radiopolyphosphates.[5—7] Ionizing radiation seems to affect the distribution of radiophosphates. In a previous work we have thoroughly investigated the oxidation of ^{32}P species induced by γ-radiation in the tripolyphosphate solution, in which the recoil ^{32}P products were found almost in monomer forms.[9] In solid target, however, the separable ^{32}P-labelled polyphosphate products were so complicated that their chromatographic patterns provided no clue to clarify the redox reaction occurring on the recoil ^{32}P.[6,9,10] The radiopolyphosphate products can be classified into five kinds, each having one ^{32}P attached as an end group.[6,7] After acid hydrolysis they undergo the following changes quantitatively.[11,12] (Blazer's notation is used.[13])

$$\overset{3}{P}\text{-O-}\overset{3}{P}\text{-} \longrightarrow 2\overset{3}{P}, \qquad \overset{2}{P}\text{-}\overset{4}{P} \longrightarrow 2\overset{3}{P},$$

$$\overset{3}{P}\text{-O-}\overset{5}{P}\text{-} \longrightarrow \overset{3}{P} + \overset{5}{P}, \quad \overset{4}{P}\text{-}\overset{4}{P} \longrightarrow \overset{3}{P} + \overset{5}{P},$$

$$\overset{5}{P}\text{-O-}\overset{5}{P}\text{-} \longrightarrow 2\overset{5}{P}$$

The apparent oxidation unmber of ^{32}P is almost unchanged even after hydrolysis into monomers. The average of the oxidation number of the total recoil ^{32}P thus can be easily estimated from the hydrolyzed monomers. A mean oxidation number of the total ^{32}P is more available than the individual ^{32}P specimen for the study of the redox reaction occurring on the recoil ^{32}P.

In the present work, sodium metaphosphate glass, a glassy polyphosphate known as Graham's salt, was used as a target to investigate the reaction of ionizing radiation on the recoil ^{32}P, since such glass can firmly trap the reactive radicals produced by the γ-radiolysis at room temperature.[14—15] In order simplify the reaction system, all the ^{32}P precursors of low oxidation state can be represented by $\overset{3}{P}$ (phosphite species) since there are only $\overset{3}{P}$ and $\overset{5}{P}$ states after hydrolysis. The "mean oxidation number" (abbreviated as "MON") is also applied as a parameter to evaluate the effects of ionizing radiation on the chemical state of the recoil product.

Experimental

Preparation of Target Materials. Graham's salt, sodium metaphosphate glass having the chemical form $(NaPO_3)_n$ was prepared as follows:

Sodium dihydrogen phosphate dihydrate was dehydrated at 800 °C for three hours in an electric furnace. The fused salt was then quenched to give a clear glass sheet with thickness of about 2 ± 0.2 mm between two brass plates. The degree of polymerization, determined by pH titration[17] and viscosity measurement,[18] showed a value between 50 and 100. In the metal-doped Graham's slat, about 0.5—3 mol percent of MnO, Sb_2O_3, Sb_2O_5 or NiO was mixed thoroughly with sodium dihydrogen phosphate dihydrate and was then treated in the same way as in the preparation of a metal containing phosphate glass.

NaI doped Grabam's salt was prepared under nitrogen atmosphere in a specially designed quartz tube.[7] The content of iodide was determined colorimetrically after being extracted into chloroform.

Irradiation. Neutron activation was carried out with the Kyoto University Reactor (KUR), with a neutron flux of *ca.* 2×10^{13} n cm^{-2} s^{-1} and a gross γ-ray dose rate of about 4.5×10^{21} eV g^{-1} hr^{-1} in the pneumatic tube, or a neutron flux of *ca.* 4×10^{12} n cm^{-2} s^{-1} and a gross γ-ray dose rate of *ca.* 2×10^{21} eV g^{-1} hr^{-1} in a slant tube.

Gamma ray irradiation was carried out with a ^{60}Co source at the Institute for Solid State Physics of University of Tokyo.

Eight positions, with γ-ray dose rate of $(3.7\pm0.1)\times10^{18}$ eV·g^{-1} hr^{-1}, around the standard source were chosen.

Chemical Analysis. In order to prevent the redox reaction induced by dissolution, the irradiated solid sample was carefully dissolved in 6 M HCl under nitrogen atmosphere. The role of HCl is not only to hydrolyze polyphosphate into monomer forms, but also to suppress the oxidation reaction induced by the color center during the course of dissolution.[15,16]

All the samples except the isothermally annealed ones were separated by anion-exchange chromatography. A gradient elution of 0.1—0.6 M ammonium acetate solution through an acetate form Dowex 1×8 anion-exchange resin of the size of 1×15 cm ϕ was applied for the separation of the phosphoxy anions of different oxidation states.[6,8]

Separation of the annealed samples was carried out by the paper chromatographic method. Toyo Roshi No. 50 filter paper was used as paper strip, and a mixture of *n*-propanol, ammonia and water in the ratio 6 : 3 : 1 in volume was used as developer. The R_f-values of the radioactive $\overset{1}{P}$, $\overset{3}{P}$ and $\overset{5}{P}$ species, determined by automatic radioactive scanning method, were found to be 0, 0.30 and 0.66, respectively. Quantitative determination of the phosphorus species was carried out colorimetrically by the molybdenum blue method[19-22]; 1 ml from each of the separated fraction was taken prior to colorimetry for the determination of radioactivity.

Results

Distribution of Radioactive Species and the Mean Oxidation Number of ^{32}P in Pure Salt. Distribution of ^{32}P species in the forms of hypophosphite ($\overset{1}{P}$), phosphite ($\overset{3}{P}$) and phosphate ($\overset{5}{P}$), obtained from the Graham's salt after hydrolysis with 6 M HCl is given in Table 1 for two independent series of experiments, A and B. The result shows that all the ^{32}P is hydrolyzed into monomer forms. The MON ^{32}P calculated from the yields of $\overset{1}{P}$, $\overset{3}{P}$ and $\overset{5}{P}$, is given in the last column of Table 1.

The MON of ^{32}P depends predominantly upon the radioactivity ratio of $\overset{3}{P}$ and $\overset{5}{P}$ species. Since the yield of radioactive $\overset{1}{P}$ is negligibly small as compared with that of $\overset{3}{P}$ and $\overset{5}{P}$, it has little effect on the evaluation of MON. The estimated mean oxidation number of ^{32}P is *ca.* +4.0, when irradiation time is shorter than 60 s. (the absorbed energy, by referring to ^{60}Co γ-ray dose, was about 6×10^{19} eV/g).

A rise of mean oxidation number of ^{32}P was observed only when the exposure of target in the nuclear reactor is sufficiently long. For instance, the mean oxidation number of ^{32}P was found to be +4.2 by 120 s irradiation, in which the target absorbed an energy dose of about 1.2×10^{20} eV/g. Such an observation indicates that the ambient radiation in the reactor is partially effective in raising the oxidation state of ^{32}P.

A color center was formed in the glass during the course of exposure in the reactor. The absorbancy at 510 nm, which attributed to trapped hole by many workers[14,16,23] increased with the exposure time (Fig. 1).

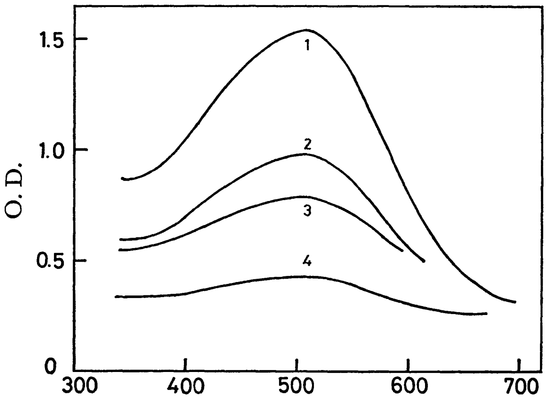

Fig. 1. Absorption spectra of reactor irradiated Graham's salts. Curves 1, 2, 3 and 4 denote irradiation times 120, 60, 30, 15 seconds in pneumatic tube.

Table 1. Distribution of radioactive hypophosphite ($\overset{1}{P}$), phosphite ($\overset{3}{P}$), and phosphate ($\overset{5}{P}$) species as well as the mean oxidation number of ^{32}P in reactor irradiated pure Graham's salt

Experiments of series A and B were carried out, independently.

Irradiation time (s)[d]	Series	Energy[a] absorbed (10^{19} eV/g)	Specific Activity (μci/g)	^{32}P yield $\overset{1}{P}$(%)	$\overset{3}{P}$(%)	$\overset{5}{P}$(%)	$\overset{5}{P}/\overset{3}{P}$	R[b] (%)	MON[c]
5	A	0.33	1.8	0.6	47.0	52.4	1.1	—	4.0
15	A	1.3	6.0	1.2	45.8	42.6	1.1	111	4.0
	B	1.5	7.5	1.6	44.1	54.3		94.9	4.0
30	A	2.8	13.6	1.4	45.9	51.6	1.1	107	4.0
	B	3.1	14.0	1.6	44.6	53.9		101	4.0
60	A	5.5	21.5	1.8	45.7	52.5	1.1	102	4.0
	B	7.2	31.0	0.9	47.5	51.6		85.6	4.0
120	A	—	51.8	2.0	35.5	62.5	1.6	—	4.2
	B	11	56.0	1.1	39.5	59.5		91.3	4.2

a) Monitrored by phosphate glass. (*i. e.* by the optical densisy of Graham's salt)[7] b) Total recovery of radioactivity with average value of 98.9%. c) Mean oxidation number of ^{32}P. d) Irradiated in pneumatic tube.

A separate series of irradiation by ^{60}Co γ-ray shows that the optical density of the phosphate glass at 510 nm obeys Beer's law at least up to 10^{19} eV/g, which is in good agreement with Kobayashi's works[7,15,16] The optical absorbancy in a higher dose region does not seem to obey Beer's law but logarithmic one.[15,16,24] It should be emphasized that the mean oxidation number of ^{32}P increases beyond critical point, turning logarithmic.

Effect of Additives on MON of ^{32}P. In order to study the effect of ambient radiation in the reactor, hole scavengers such as Mn^{2+}, Sb^{3+} and I^- as well as electron scavengers such as Ni^{2+} and Sb^{5+} were doped individually from 0.5 to 3.0 mol% into Graham's salt. They were all irradiated in the slant tube together with a pure salt for about 6 min.

These glasses doped with hole scavenger always showed no absorption at 510 nm even after having absorbed a radiation energy *ca.* 10^{21} eV/g. The mean oxidation number of ^{32}P remained at 3.96—4.02, while that of ^{32}P in pure salt was found to be 4.25. The value on pure salt is also expected (Table 1), if we compare the energies absorbed. On the other hand the mean oxidation number of ^{32}P in these Ni^{2+}- and Sb^{5+}-doped salts were found to be +4.22 and 4.12, respectively. This value of MON for ^{32}P is very close to that observed in the pure salt which was irradiated under the same conditions. The detail of the experimental results are summarized in Table 2 (a) for both the distribution of ^{32}P species and its mean oxidation number. The results show that the oxidation of ^{32}P products might be due to the trapped hole. The reaction of electron is not clear, though electron may form oxygen center and reacts as an oxidant.[7,15,25,26]

The yields of the recoiled monoatomic ^{32}P species obtained merely by dissolving the irradiated glass into pure water without hydrolysis, are also given in the forms of $\overset{1}{\text{P}}$, $\overset{3}{\text{P}}$ and $\overset{5}{\text{P}}$ in Table 2 (b). The radioactivity involved in the monoatomic ^{32}P fractions was less than 10% except Sb^{3+}- and Sb^{5+}-doped glasses in which it was near 20%. As a matter of fact, more than 90% of the recoil ^{32}P was labelled into the polyphosphate.[6,7] The mean oxidation number of ^{32}P in such monoatomic ^{32}P product, however, kept a comparatively low value *ca.* +3.0, independent of the dopants. Both trapped hole and electron has little effect on such recoiled monoatomic ^{32}P species.

Table 2. Mean oxidation number of ^{32}P in doped Graham's salt

Irradiated samples were treated in two ways before chemical analysis:
(a) hydrolyzed with 6M HCl,
(b) dissolved in water without hydrolysis.

Ion doped (mol %)	$\overset{1}{\text{P}}$(%)	$\overset{3}{\text{P}}$(%)	$\overset{5}{\text{P}}$(%)	MON
(a) Hydrolyzed sample				
Mn^{2+} (2)	1.2	48.6	50.2	3.98
Sb^{3+} (2)	4.4	42.8	52.7	3.96
I^- (5)	0.8	47.2	52.0	4.02
Sb^{5+} (2)	—	44.0	56.0	4.12
Ni^{2+} (0.5)	1.9	37.4	61.7	4.22
pure salt	—	37.4	62.6	4.25
(b) Unhydrolyzed sample				
Mn^{2+}	0.4	4.4	1.0	3.2
Sb^{3+}	8.2	3.3	8.6	3.0
I^-	0.6	8.5	—	2.9
Sb^{5+}	5	4	5	2.9
pure salt	0.8	5.0	1.2	3.3

All samples were irradiated together in the slant tube for about 6 min. corresponding to a γ-energy of *ca.* 10^{20} eV/g.

Effects of γ-Ray Annealing on Recoil ^{32}P. Further studies of the radiation effect on ^{32}P were carried out by ^{60}Co source prior to neutron activation. After having absorbed an energy of about 10^{20} eV/g (approximately the order of energy which the target might absorb during its exposure in the reactor), the colored glasses were irradiated together with the untreated Graham's salts in the pneumatic tube. The results are illustrated in Figs. 2 (a) and (b) in terms of the radioactivity growth of $\overset{3}{\text{P}}$ and $\overset{5}{\text{P}}$ as a function of irradiated time. The yields of radioactive $\overset{1}{\text{P}}$ are always as low as 1% of the total activity, remaining virtually unchanged. The gamma ray treated samples always had higher $\overset{5}{\text{P}}$ activity and lower $\overset{3}{\text{P}}$ activity than the untreated ones. This indicates that the ionizing radiation may partially induce the oxidation of the recoil ^{32}P species and pre-neutron irradiation γ-ray treatment can enhance such a reaction. This evidence is more clearly confirmed in Fig. 3. The $\overset{5}{\text{P}}/\overset{3}{\text{P}}$ ratio and the mean oxidation number of ^{32}P for both series are shown as functions of the absorbed energy in Fig. 3 (a) and (b), respectively. The γ-ray treated sample always

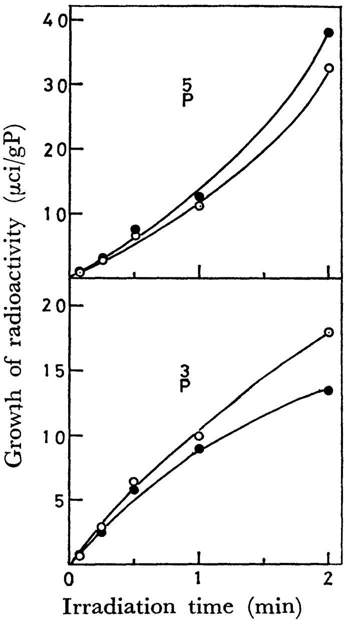

Fig. 2. Growth of the specific activities of $\overset{3}{\text{P}}$ and $\overset{5}{\text{P}}$ fractions in neutron activated Graham's salt.
-○-: Uutreated salt. -●-: Target was irradiated by ^{60}Co γ-ray with a dose of obout 10^{20} eV/g before neutron activation.

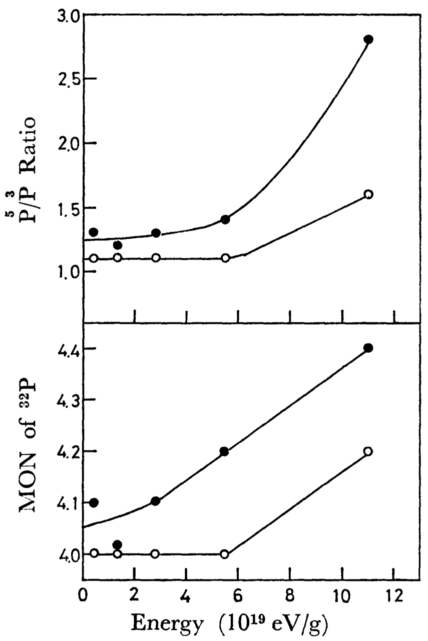

Fig. 3. Variations of MON of ^{32}P and the radioactive $\overset{5}{P}/\overset{3}{P}$ ratio as function of energy absorbed in the reactor.
-O-: Untreated sample, -●-: Target was irradiated by 10^{20} eV/g before neutron activation.

kept higher $\overset{5}{P}/\overset{3}{P}$ ratio and the mean oxidation number of ^{32}P than those of the untreated sample, the difference increasing with energy. The oxidation induced by γ-radiation seems to have a threshold of energy. From the curves of untreated sample (Fig. 3), when energy absorbed was less than 6×10^{19} eV/g, the reaction does not seem able to occur. The oxidation would occur only after the target absorbed enough energy which might exceed 6×10^{19} eV/g.

The post-neutron irradiation γ-ray annealing was studied within the γ-ray dose ranging from 1.4×10^{20} to 1.9×10^{21} eV/g. The results are given in Fig. 4 in terms of the MON of ^{32}P and the yields of radioactive $\overset{5}{P}$ and $\overset{3}{P}$. In contrast to the pre-neutron annealing curves (Fig. 3) the post-neutron annealing curves (Fig. 4) show an opposite trend in the oxidation of ^{32}P. The reaction is rapid in the beginning, but becomes slow with the increase in radiation dose. It seems very difficult for the mean oxidation number of ^{32}P to retain the valence state +5 of the target phosphorus by the gamma ray annealing.

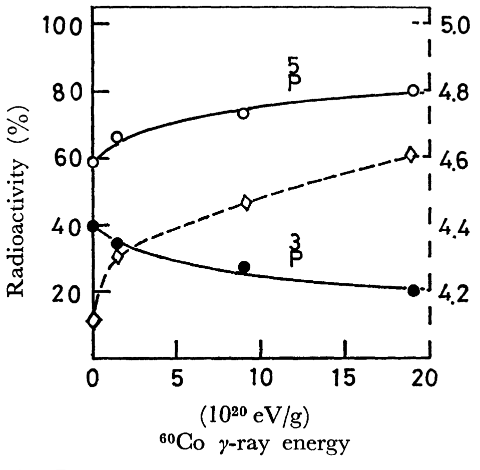

Fig. 4. Post-neutron irradiation ^{60}Co γ-ray annealing curves for radioactive $\overset{3}{P}$ and $\overset{5}{P}$ fractions. Dotted line denotes the variation of MON of ^{32}P as function of γ-ray energy.

Effects of Thermal Annealing on Recoil ^{32}P. Thermal annealing of the reactor irradiated glass was carried out at 50, 100, 200, 250, 300 and 400 °C. The results are summarized in Table 3.

The isothermal annealing curves at each temperature are given in Fig. 5. Paper chromatographic scanning was made for the two major components, $\overset{3}{P}$ and $\overset{5}{P}$ of ^{32}P products, from the hydrolyzed acidic solution (6M HCl) of the annealed sample. The detectable $\overset{1}{P}$-activity was always less than one percent, almost completely disappearing at 300 °C. No matter what the annealing temperature was, within 2—5 min, the yield of ^{32}P components attained rapidly a fixed ratio between $\overset{3}{P}$ and $\overset{5}{P}$. The higher the annealing

TABLE 3. THERMAL ANNEALING OF THE REACTOR IRRADIATED GRAHAM'S SALT

Annealing temperature (°C)	Annealing time (min)					Change of Color
51±1	5	10	20	40	60	brown
101±2	5	10	20	40	60	brown
199±3	5	10	20	40	60	colorless
250	5	10	30	60		colorless
300±2	5	10	20	20	40	colorless
396±2	2[a]	5	10	15		white

a) colorless.

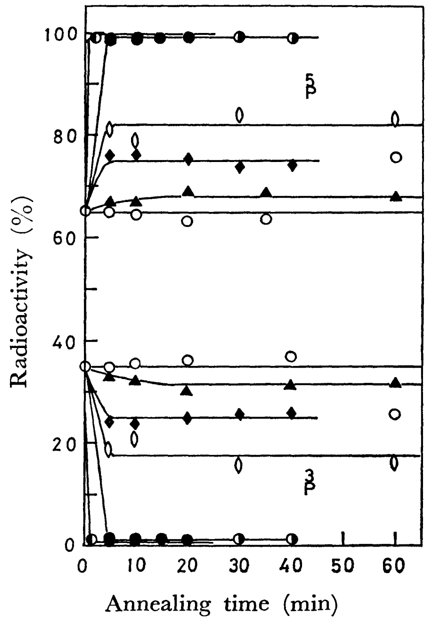

Fig. 5. Isothermal annealing curves of radioactive $\overset{3}{P}$ and $\overset{5}{P}$ fractions in reactor irradiated Graham's salt. O: 50°, △: 100°, ◆: 200°, O: 250°, ◑: 300° and ◐: 400 °C.

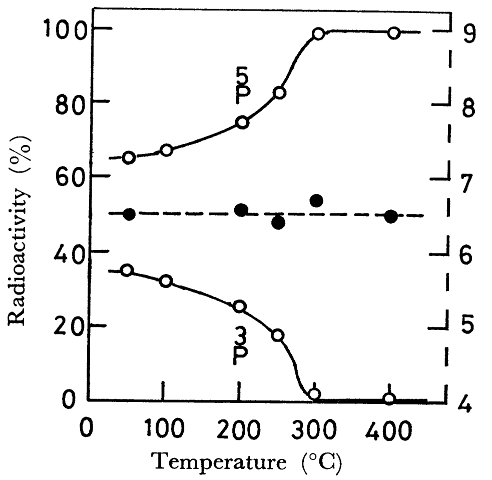

Fig. 6. Isochronic curves of radioactive $\overset{3}{\mathrm{P}}$ and $\overset{5}{\mathrm{P}}$ fractions. The total specific activities detected at each annealing temperature are also presented in dotted line.

temperature, the more rapidly the isothermal curves reached its equilibrium. Such stationary composition of ^{32}P products at each annealing temperature maintained some 60 min.

In Fig. 6, the radioactive yields of both $\overset{3}{\mathrm{P}}$ and $\overset{5}{\mathrm{P}}$, estimated at the stationary state of each isothermal curve, are plotted against the annealing temperature along with corresponding specific activity detected at the same temperature. A rapid increase (or decrease) of $\overset{5}{\mathrm{P}}$ (or $\overset{3}{\mathrm{P}}$) yield was observed from 200 °C and finally the yield of $\overset{5}{\mathrm{P}}$ (or $\overset{3}{\mathrm{P}}$) became closer to hundred (or null) percent by 300 °C. This range of temperature (200—300 °C) just covers the decomposition temperature of the low oxyphosphorus compounds such as phosphite.[11] In the case that decomposition occurs, a part of the ^{32}P would escape in the gaseous phosphine species,[27,28] and thus the detectable specific activity would decrease with the temperature from 200 °C. However, the specific activity curve (Fig. 7) showed no change even when the sample was heated up to 400 °C. All the ^{32}P were converted into penta-valence by thermal annealing. The rate of conversion of $\overset{3}{\mathrm{P}}$ into $\overset{5}{\mathrm{P}}$ was estimated from the slope for each annealing curve (Fig. 5). This conversion rate was used for the Arrhenius plot to estimate the activation energy of this particular system. A straight line of such a plot is shown in Fig. 7, an activation energy of 7.1 kcal/mol being obtained.

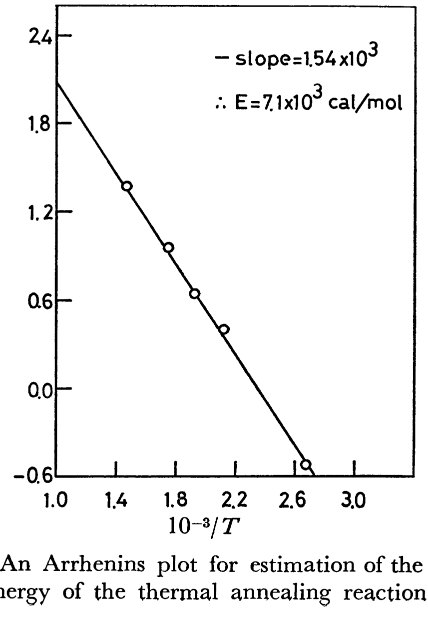

Fig. 7. An Arrhenins plot for estimation of the activation energy of the thermal annealing reaction.

A comparison was made between the fading in color and the change in mean oxidation number of ^{32}P in order to investigate the correlation between the trapped hole (the color center) and the oxidation of ^{32}P species (Fig. 8). The optical absorbancy at 510 nm attributed to the trapped hole[14,23] disappeared completely with the temperature range 100—200 °C. However, the rise of the mean oxidation number of ^{32}P between 100—200 °C was very gradual. It rose sharply from 200 °C and attained +5 by 300 °C (dotted line, Fig. 8).

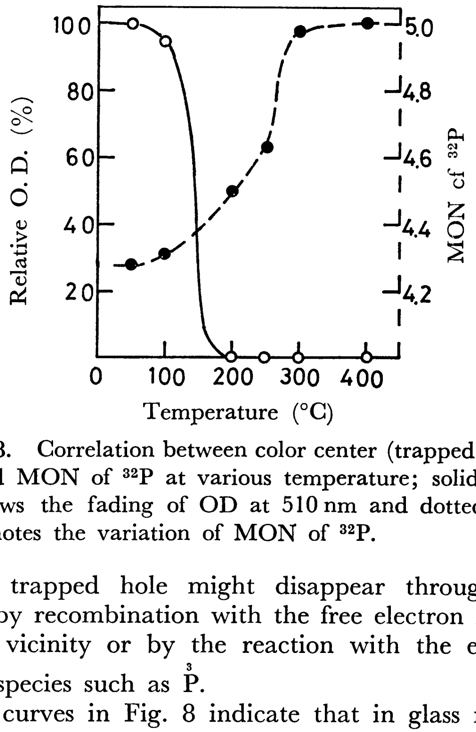

Fig. 8. Correlation between color center (trapped hole) and MON of ^{32}P at various temperature; solid line shows the fading of OD at 510 nm and dotted line denotes the variation of MON of ^{32}P.

The trapped hole might disappear through two ways; by recombination with the free electron located in the vicinity or by the reaction with the electron donor species such as $\overset{3}{\mathrm{P}}$.

The curves in Fig. 8 indicate that in glass matrix, though the oxidation of ^{32}P species by the trapped hole is not impossible, it is not a predominant reaction. Disappearance of the color center is mainly due to its recombination with electron or negative ion during thermal annealing.

Discussion

During ^{31}P(n, γ) ^{32}P recoil in polyphosphate, all the ^{32}P are freed from their bonding to become a monomer which is often deficient in oxygen.[7,29] However, in the spiral shape of polyphosphate molecule, about 90% of the recoil ^{32}P undergoes recombination to reform radioactive polyphosphate with one ^{32}P as end group which, compared with the monoatomic ^{32}P product, is fairly rich in oxygen[7]. Hence the mean oxidation number of ^{32}P in polymer forms is always higher than that in monomer forms$^{30)}$. Ionizing radiation might cause the oxidation of the recoil ^{32}P product. Such oxidation seems to be an electronic process since it can be suppressed by the electron donor (Table 3 (a)). The γ-radiolysis of phosphate glass can be simplified as follows.

$$\underset{\text{(glass)}}{G} \rightsquigarrow \underset{\text{(trapped hole)}}{G^+} + \underset{\text{(electron)}}{e^-}$$

Subsequent reaction might occur between G$^+$ and hole scavenger(S):

$$G^+ + S \longrightarrow G + S^+$$

If there is no such electron donor as hole scavenger, G$^+$ may react with recoil ^{32}P species of lower chemical state; for instance:

$$G^+ + \overset{3}{P} \longrightarrow G + \overset{4}{P}$$

which apparently raises the mean oxidation number of ^{32}P. However, such an oxidation is partial and greatly depends on the concentrations of both the trapped holes and ^{32}P. Another possibility for raising the mean oxidation number by radiation is OH radical from water molecule$^{30)}$. In such a radiolytic achievement, phase effects play an important role. The post-neutron irradiation γ-ray annealing shows an entirely different behavior between solid and aqueous targets. The mean oxidation number of ^{32}P observed in solid target increases only from +4.1 to +4.6 by absorbing an energy even higher than 10^{21} eV/g.$^{7)}$ Such discrepancy in oxidation reaction may be due to the different diffusion rates of the reactants in solid and liquid phases. The higher diffusion rate and concentration of OH radical in liquid state give rise to a more rapid and complete oxidation of the recoil ^{32}P product in aqueous target than in solid target.

The effect of diffusion phenomena on the oxidation of recoil product in the solid target can be elucidated by annealing. Isochronic curves (Fig. 6) indicate that within the temperature range 200—300 °C, all the recoil ^{32}P products are converted into $\overset{5}{P}$ state. The temperature range gives no definite correlation with the temperature for disappearance of the color center (positive defects) which disappeared completely by 100 °C (Fig. 8). The activation energy of the annealing is about 0.3 eV (7.1 kcal/mol). This value of activation energy seems to demonstrate that the thermal annealing reaction is not an electronic but a diffusion process. The potential well of the trapped hole (color center) produced by the γ-radiolysis in the glass is about 0.3 eV which is ten times as low as the optical activation energy 2.6 eV (510 nm). The following conclusion can be made for the annealing effects. In the reactor irradiation, two kinds of abnormal domains are produced and localized in the solid target, a) the recoil site (or hot zone) which involves radioactive product and many other reactive fragments, and b) the radiation spur which contains positively and negatively charged species (color centers). During the course of annealing, within the first domain, hot zone, the recoil product may react with its surrounding reactive fragments to raise the retention value.$^{31)}$ Within the second domain, radiation spur, the interaction between the positive and negative defects also takes place.$^{32,33)}$ Interactions between the recoil product and the color centers are possible. However, before the trapped species in the radiation spur diffuse to react with the recoil product which is considerably far away, they have already reacted one another within the domain (radiation spur). This is why the temperature of the complete disappearance of the color center and that of the oxidation of the recoil product do not coincide (Fig. 8).

References

1) L. Lindner and M. Harbottle, "Chemical Effects of Nuclear Transformation," Vol. p. 485, IAEA, Vienna (1961).

2) J. Fenger, *Radiochim. Acta,* **12**, 186 (1969).

3) J. Fenger, *ibid.*, **16**, 42 (1971).

4) J. Fenger and P. B. Pagsberg, *J. Inorg. Nucl. Chem*, **35**, 31 (1973).

5) N. Matsuura, N. Shinohara, and T. K. Lin; *ibid.*, **31**, 1251 (1969).

6) N. Matsuura and T. K. Lin, *ibid.*, **32**, 353 (1970).

7) T. K. Lin, Dissertation, The University of Tokyo. (1972).

8) N. Matsuura and T. K. Lin, *J. Inorg. Nucl. Chem.*, **33**, 2281 (1971).

9) T. Nakamura, K. Ujimoto, N. Yoza, and S. Ohashi, *ibid.*, 32, 3191 (1970).

10) M. Tominaga, T. Nakamura, and S. Ohashi, *ibid.*, 34, 1409 (1972).

11) S. Ohashi, "Topics in Phosphorus Chemistry," Vol. 1, p. 113 Interscience Pub. New York (1974).

12) Van Wazer, "Phosphorus and Its Compounds," Vol. 1, Interscience Pub., New York (1962), p. 390.

13) B. Blazer and K. H. Worms, *Z. Anorg. Allg. Chem.*, **300**, 225 (1959).

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

15) Y. Kobayashi, A. Barkatt, and J. Rabani, *J. Phys. Chem.*, **78**, 752 (1974).

16) Y. Kobayashi, Dissertation, The University of Tokyo (1975).

17) Ref. 12, pp. 419, 717.

18) N. Matsuura, T. K. Lin, and Y. Kobayashi, This Bulletin, **43**, 2850 (1970).

19) N. Matsuura and Y. Kurimura, *Bunseki Kagaku*, **16**, 622 (1967).

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

21) N. Yoza and S. Ohashi, This Bulletin, **37**, 33 (1964).

22) N. Yoza and S. Ohasi, *ibid.*, **37**, 37 (1964).

23) Y. Kobayashi and N. Matsuura, *ibid.*, **46**, 1346 (1973).

24) Y. Kobayashi and N. Matsuura, *Chem. Lett.*, **1975**, 1.

25) J. L. Baptista, G. W. A. Newton, and V. J. Robinson, *Trans. Faraday Soc.*, **64**, 462 (1968).

26) T. Andersen and J. L. Baptista, *ibid.*, **67**, 1213 (1971).

27) Ref. 12, p. 379.

28) Clement Duval, "Inorganic Thermogravimetric Analysis," 2nd Ed. Elsevier (1963), p. 201.

29) D. L. Bunker and G. V. Volkenburgh, *J. Phys. Chem.*, **74**, 2193 (1970).

30) T. K. Lin, *Nucl. Sci. J.*, to be published.

31) G. Harbottle and N. Sutin, *Adv. Inorg. Chem. Radiochem.*, **1**, 267 (1959).

32) J. H. Thompson and W. Miller, *J. Chem. Phys.*, **38**, 2477 (1963).

33) C. Bettinali and P. Granati, *Z. Phys. Chem. N. F.*, **70**, 24 (1970).