BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 2779—2787 (1967)

Hot Atom Chemistry of Phenylphosphorus Compounds

Yoshiyuki KISO, Mitsue KOBAYASHI, Yoshinori KITAOKA,
Keizo KAWAMOTO and Jitsuya TAKADA

Research Reactor Institute, Kyoto University, Kumatori-cho, Sennan-gun, Osaka

(Received June 27, 1967)

A series of phenylphosphorus compounds, such as triphenylphosphine, triphenylphosphine oxide, triphenylphosphite, diphenylphosphite, tricresylphosphite, monophenylphosphate, triphenylphosphate, phenylphosphonic acid and phenylphosphonous acid, were irradiated in a nuclear reactor for 15—2100 min with a thermal neutron flux of 5×10^{12} n/cm^2/sec. The relative amounts of the ^{32}P-labeled gaseous products and the products soluble in an aqueous solution in the irradiated samples were then estimated. It was found that the compounds containing an oxygen atom bonded as P=O in a molecule had a tendency to yield the higher percentages of the products which were nonvolatile and soluble in an aqueous solution. The recoil products were separated into components by paper chromatography, and the chemical form of each component was identified. It was shown that the number of recoil products separated and the distribution of the chemical forms were greatly influenced by the chemical forms of the target compounds. The chemical reactions of the recoil ^{32}P atom are also discussed, and a mechanism of the reactions which fits the experimental results is proposed.

The first study of the Szilard-Chalmers reaction in a phosphorus compound was made over a quarter of a century ago.1) A benzene solution of triphenylphosphate was then irradiated with thermal neutrons, and the fate of the ^{32}P atom produced by the ^{31}P(n, γ)^{32}P reaction was investigated using a solvent extraction technique. After that, many works on the recoil chemistry of ^{32}P have been reported. The neutron irradiation of phosphorus oxyacids has shown that most of the ^{32}P in the recoil products is in the same oxidation state as in the parent compound.2)

---

1) O. Erbacher and K. Philipp, *Z. Physik. Chem. (Leipzig)*, **A179**, 263 (1937).

2) a) K. Yoshihara and T. Yokoshima, This Bulletin, **34**, 123 (1961); b) P. A. Sellers, T. R. Sato and H. H. Strain, *J. Inorg. Nucl. Chem.*, **5**, 31 (1957); c) T. R. Sato, P. A. Sellers and H. H. Strain, *ibid.*, **11**, 84 (1959); d) L. Lindner and G. Harbottle, "Chemical Effects of Nuclear Transformations," Vol. 1, International Atomic Energy Agency, Vienna (1961), p. 485; e) M. Shima and S. Utsumi, *J. Inorg. Nucl. Chem.*, **20**, 177 (1961).

Relatively little is known, however, about the chemical effects of the nuclear reaction of organic phosphorus compounds. Though trimethylphosphine,³⁾ triphenylphosphine,⁴⁾ triphenylphosphine oxide,⁵⁾ triphenylphosphate⁶⁾ and tri-*n*-butyl phosphate⁷⁾ have been subjected to neutron irradiation and the recoil products have been analyzed independently, it remains unsettled how the kinds and number of the recoil products are influenced by the chemical form of the target materials. This report will give informations concerning the effects of the chemical form of the target materials on the distribution of ^{32}P among the various recoil products which are produced in the neutron-irradiated phenylphosphorus compounds, such as triphenylphosphine, triphenylphosphine oxide, triphenylphosphite, tricresylphosphite, diphenylphosphite, triphenylphosphate, monophenylphosphate, phenylphosphonic acid, and phenylphosphonous acid.

Experimental

Materials. Triphenylphosphine was prepared by reacting phosphorus trichloride with phenylmagnesium bromide, followed by recrystallization from water; mp 78.5°C. Triphenylphosphine was oxidized with aqueous bromine to triphenylphosphine oxide. The product was recrystallized from ethyl alcohol and a mixture of benzene-ligroin (1 : 1), and dried on concentrated sulfuric acid; mp 157°C. Chemicals of the Katayama Kagaku Co., Ltd., triphenylphosphate (from ethyl alcohol, mp 51°C), monophenylphosphate (from chloroform, mp 99.5°C), phenylphosphonic acid (from water, mp 160°C), and phenylphosphonous acid (from water, mp 80°C), were purified by thrice recrystallizations. Triphenylphosphite, tricresylphosphite, and diphenylphosphite were also purchased from the Katayama Kagaku Co., Ltd.; they were used without further purification.

Neutron Irradiation. The weighed samples (*ca.* 100 mg) to be irradiated were sealed in polyethylene tubes (inside dia. 2 mm) and irradiated with a thermal neutron flux of 5×10^{12} n/cm²·sec in a pneumatic tube of KUR.⁸⁾ The cadmium ratio at the irradiation site was 5.7, the γ-dose rate at 1 MW operation was 2.7×10^{7} R/hr, and the temperature was about 40°C. Irradiation was carried out for 15—90 min. Triphenylphosphine, triphenylphosphine oxide, triphenylphosphite, and triphenylphosphate were irradiated in a hydrolytic tube with a flux of 2×10^{13} n/cm²·sec for 9 hr. The cadmium ratio at the position was 4.0, and the γ-dose rate was 3×10^{7} R/hr. In this case, a sample tube of quartz (dia. 3 mm) was used.

Irradiation at a temperature near that of dry ice was carried out for 15 min in the pneumatic tube. A sealed polyethylene tube containing 100 mg of a sample was cooled by dry-ice in a larger polyethylene tube.⁹⁾ After irradiation, the sample was kept at the dry-ice temperature during the time of storage.

γ-Ray Irradiation. To check the decomposition of a sample by γ-ray irradiation in the reactor, the phosphorus compounds were irradiated for 4 hr by the use of a ^{60}Co γ-ray source of 7000 Ci.¹⁰⁾ The dose rate of the position was 2.5×10^{6} R/hr. The irradiated sample was then analyzed by chromatography. No decomposition of the sample was detected by the neutron activation analysis of the chromatographed strip.

Separation Method and Measurement of Radioactivity. After having been cooled for a week, the irradiated sample was shaken with a mixture of chloroform and water (1 : 1 in volume); the radioactivity in each layer was then measured. The recoil products were also separated paperchromatography on Toyoroshi No. 50 filter-paper (2×40 cm) by the ascending method for 15 hr. As solvents, (A) propanol-ammonia-water (6 : 3 : 1 in volume),¹¹⁾ (B) butanol-propionic acid-water,¹²⁾ and (C) phenol-water¹²⁾ were examined. Almost all the experiments were, however, carried out using solvent (A) because it was most preferable for the separation of radioactive phosphorus compounds. After development, the paper strips were dried up in warm air, and the distribution of radioactivity was examined by autoradiography using Fuji

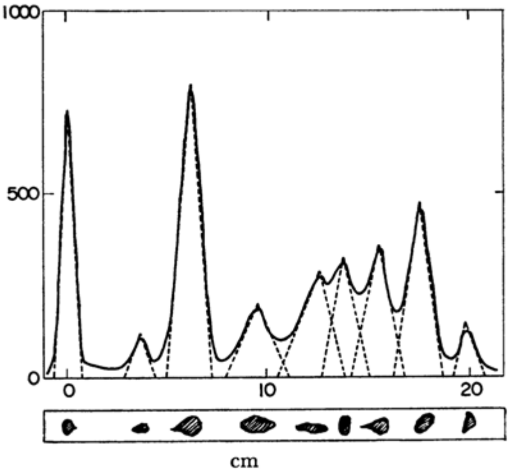


Fig. 1. Autoradiograph of radioactive products and distribution of ^{32}P on a paper chromatogram in $C_6H_5P{=}O\cdot H\cdot(OH)$.

---

3) M. Halmann and L. Kugel, *J. Inorg. Nucl. Chem.*, **25**, 1343 (1963).

4) M. Halmann, "Chemical Effects of Nuclear Transformations," Vol. 1, International Atomic Energy Agency, Vienna (1961), p. 195.

5) V. D. Nefedov, E. N. Sinotov and M. A. Tropova, *Radiokhimiya*, **1**, 236 (1959).

6) a) H. Drawe and A. Henglein, *Z. Naturforsch.*, **17b**, 486 (1962); b) A. A. Gordus and C. H. Hsiung, *J. Chem. Phys.*, **36**, 954 (1962).

7) K. E. Siekierska, A. Halpen and A. Siuda, "Chemical Effects of Nuclear Transformations," Vol. 1, International Atomic Energy Agency, Vienna (1961), p. 171.

8) Kyoto University Reactor,

9) The temperature of the sample was proved to be below −20°C under irradiation for 20 min by measurement with a copper-constantan thermocouple.

10) This source belongs to the Radiation Center of Osaka Prefecture.

11) T. Weil, *Helv. Chim. Acta*, **28**, 1274 (1955).

12) A. A. Benson, J. A. Bassham, M. Calvin, T. C. Goodle, H. A. Hass and W. Stepka, *J. Am. Chem. Soc.*, **72**, 1710 (1950).

medical X-ray film (27.9×35.6 cm). Quantitative determination of the radioactivity on the chromatographed strip was made by an autoradioscanner. A typical example of the scanning curves obtained is shown in Fig. 1. By comparing the cruve with the autoradiogram of the sample in Fig. 1, the relative amount of each separated component could be evaluated. The scanning curve clearly shows 9 peaks corresponding to the autoradiograph pattern, but some components overlap each other in the scanning curve. Therefore, the curve was analyzed into 9 Gaussian curves in order to estimate the percentage of each component; these curves are shown by the broken lines in Fig. 1.

The standard R_f values of phosphorus compounds were also obtained for Solvent (A).

The samples irradiated in the hydrolytic tube gave many solid products that were soluble neither in chloroform nor in water. It was assumed that they contained a considerable amount of red phosphorus. The present research was, however, made only on those products which were soluble in chloroform or water.

Measurement of Radioactive Phosphine. As a gaseous recoil product, ^{32}P-labeled phosphine may be produced by the irradiation. The relative amount of phosphine was conventionally evaluated by the following procedures. Chloroform or aqueous solutions of samples (0.5 mol/*l*) were prepared at 25°C. An aliquot (1—5 μl) of the solution was taken up by a micropipette and dropped at the center of a filter paper (2×2 cm). After the vaporization of the solvent, the strip, shielded with a polyethylene sheet, was irradiated for 30 min, together with a filter paper; it thus absorbed a known amount of sodium phosphate, which was used standard sample. After the sample had cooled for a week, the radioactivity on the irradiated papers was measured by using GM counter. The relative amount of the gaseous product was then estimated from the residual radioactivity on the filter paper.

Results and Discussion

The relative amounts of radioactive phosphine produced are shown in Table 1. In triphenylphosphine oxide, phenylphosphonic acid, phenylphosphonous acid,[13] and phosphates which contain an oxygen atom double-bonded to the phosphorus atom (P=O oxygen) in a molecule, only a small percentage of the total radioactivity is due to phosphine. However, in triphenylphosphine and phosphites, the percentage of the product reaches nearly 20%.

TABLE 1. FORMATION OF ^{32}P-LABELED GASEOUS PRODUCTS

Target	Gaseous products* %
$(C_6H_5)_3P$	12.4±0.2
$(C_6H_5O)_3P$	12.2±0.2
$(CH_3C_6H_4O)_3P$	18.6±3
$(C_6H_5O)_2POH$	6.3±3.7
$(C_6H_5)_3P=O$	3.2±0.1
$(C_6H_5O)_3P=O$	0 ±0.1
$C_6H_5OP=O(OH)_2$	0 ±0.1
$C_6H_5P=O(OH)_2$	0 ±0.1
$C_6H_5P=O\cdot H\cdot(OH)$	0 ±0.1
Na_3PO_4	0 ±0.1

* The ratio was calculated from sodium phosphate as a standard compound.
The irradiation condition was at a neutron flux of 5×10^{12}n/cm^2/sec for 30 min.

Figure 2 shows the relationship between the percentage of the aqueous extract of recoil products and the irradiation time. The irradiation for 15 min has a large value and the extraction curve slowly decreases with an increase in the irradiation time, while the extraction ratios among the compounds were not remarkably changed by the irradiation time. The percentage of the extract is larger in triphenylphosphine oxide and phosphates than in triphenylphosphine and phosphites. These results show that the compounds containing an oxygen atom bonded as O=P have a tendency to yield recoil products which are nonvolatile and soluble in an aqueous solution.

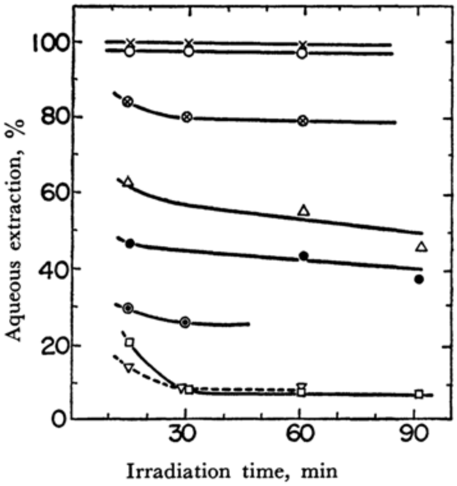


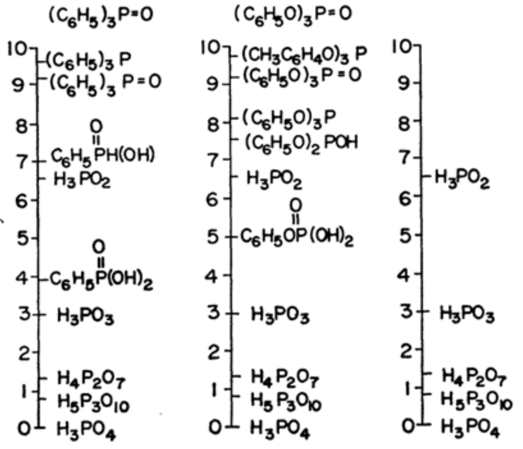
Fig. 2. Extraction of recoil products as a function of the irradiation time.

Thermal neutron flux: 5×10^{12} n/cm^2/sec
Irradiation time: 15—90 min
Irradiated samples:
×···$C_6H_5P=O(OH)_2$; ○···$C_6H_5OP=O(OH)_2$;
⊗···$C_6H_5P=O\cdot H\cdot(OH)$; △···$(C_6H_5)_3P=O$;
●···$(C_6H_5O)_3P=O$; ⊙···$(C_6H_5O)_2POH$;
▽···$(C_6H_5O)_3P$; □···$(C_6H_5)_3P$

The standard R_f values of the phosphorus compounds for the (A) solvent are given in Fig. 3. The left line in Fig. 3 shows the R_f values of phosphine

---

[13] Two chemical forms, $C_6H_5P=O\cdot H\cdot(OH)$ and $C_6H_5P(OH)_2$, have been reported for phenylphosphonous acid. Recently the monobasicity of the acid was proved in our laboratory by an electrophoretic technique. Accordingly, the structure of the acid can safely be said to be of the $C_6H_5P=O\cdot H\cdot(OH)$ form (*J. Chromatog.*, in press.).



Standard R_f of recoil products

Fig. 3. Standard R_fs of ^{32}P-labeled recoil products. Ascending solvent is a mixture of propanol-ammonia-water (6 : 3 : 1).
Left line: Phosphine and phosphine oxide derivatives
Middle line: Phosphite and phosphate derivatives
Right line: Phosphorus oxyacids.

or phosphine oxide derivatives; the middle line, those of phosphite or phosphate derivatives, and the right line, of those of phosphorus oxyacids.

The percentage of each component of ^{32}P-labeled products, as evaluated from a scanning curve, is shown schematically in the following figures. Each component is identified by the R_f values in Fig. 3. Figure 4 shows the distribution patterns of the recoil products of triphenylphosphine for various irradiation times. At a short irradiation time, the number of the components separated is as large as ten, but the number decreases with a lengthening of the irradiation time. Similar results have been obtained for all the other target materials. All the disappearing components at a long irradiation time have lower R_f values and may be assigned to hydroxylic phosphorus compounds which are soluble in water. This fact agrees with the extraction data given in Fig. 2. Since triphenylphosphine, which contains no oxygen atom in a molecule, gives a considerable amount of inorganic phosphorus products at a short irradiation time, it is assumed that the recoil ^{32}P atom reacts not only with a target material or a molecular fragment produced from it, but also competitively with oxygen molecule absorbed in the sample until all the absorbed oxygen molecules have been consumed.

If the above assumption is valid, the relative amounts of the products soluble in an aqueous solution must decrease with a lengthening of the irradiation time. The experimental results coincide with this assumption, as is shown in Fig. 2. It is also supporting evidence that the most rapid decrease in the curve in Fig. 2 is observed for triphenylphosphine, that has no oxygen atom in the molecule.

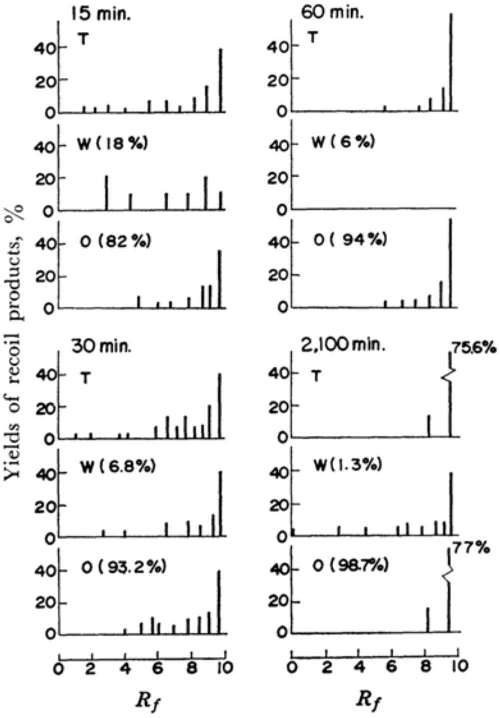


Fig. 4. Distribution of ^{32}P-labeled recoil products in irradiated $(C_6H_5)_3P$ at various irradiation times.

Thermal neutron flux: 5×10^{12} n/cm^2/sec
Irradiation time: 15—2100 min
T: Distribution of total activities.
W: Distribution of activities parted in aqueous layer.
O: Distribution of activities parted in $CHCl_3$ layer.
The relative activities parted in each layer for total activities are shown in parenthesisses.

A variety of distribution patterns among the target materials are given in Fig. 5, in which the effect of the absorbed oxygen molecule is ignored for the case of a long irradiation time. It is clear that the distribution pattern of recoil products is quite dependent on the chemical form of the target materials.

By comparing the recoil products of triphenylphosphine with those of triphenylphosphite, it is clear that the number of components separated is larger in the target materials with a phenoxy group. The ^{32}P distribution pattern is also influenced by the irradiation temperatures as is shown in Fig. 6. At a dry-ice temperature, the components of R_f zero were increased. Most of them are parted in the chloroform layer and are identified as elementary phosphorus. On the other hand, the yield of the labeled target compound was decreased.

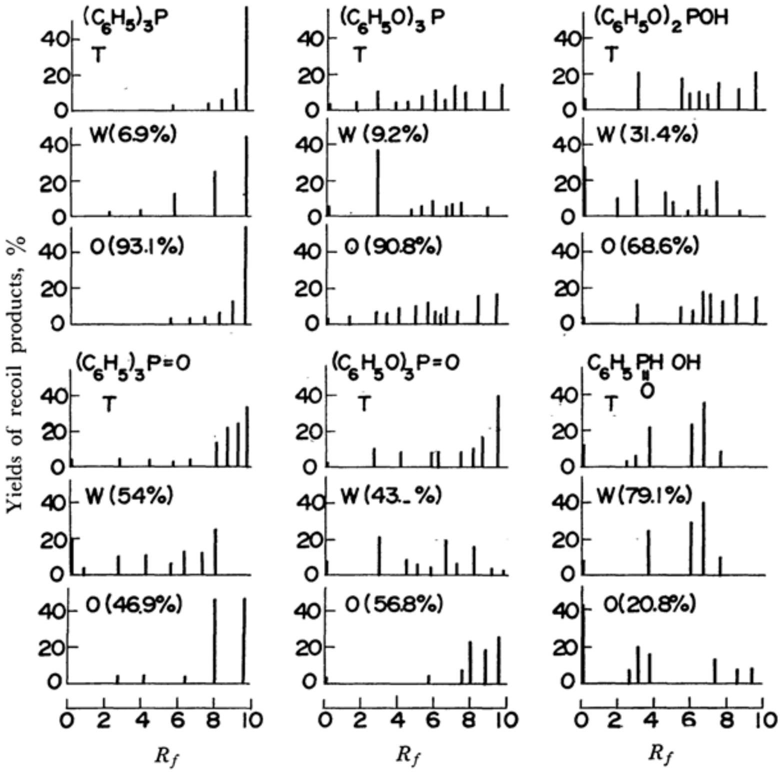


Fig. 5. The variety of the distribution of radioactive recoil products among irradiated compounds.

Thermal neutron flux: 5×10^{12} n/cm²/sec
Irradiation time: 60 min

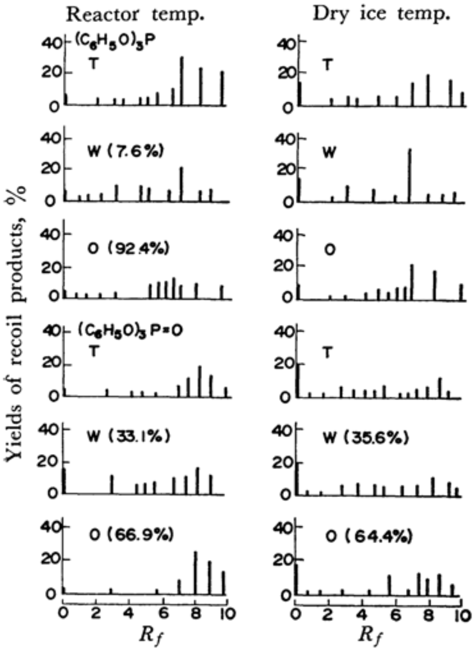


Fig. 6. Distribution of recoil products at reactor temperature and dry ice temperature.

Thermal neutron flux: 5×10^{12} n/cm²/sec
Irradiation time: 15 min.

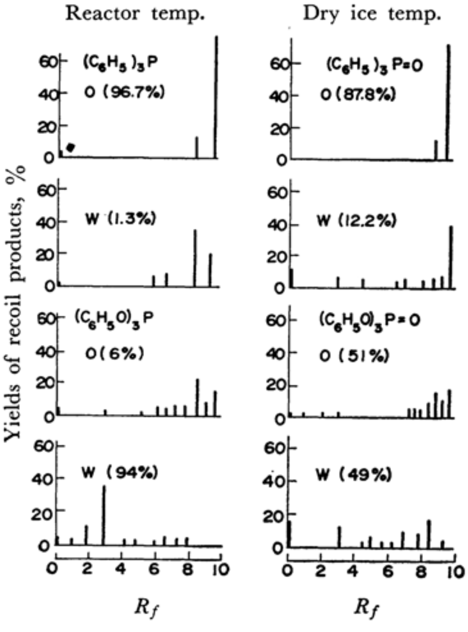


Fig. 7. Distribution of radioactive products.

Thermal neutron flux: 2×10^{13} n/cm²/sec
Irradiation time: 9 hr

Figure 7 shows the distribution patterns of the recoil products at a long irradiation time in the hydrolytic tube.

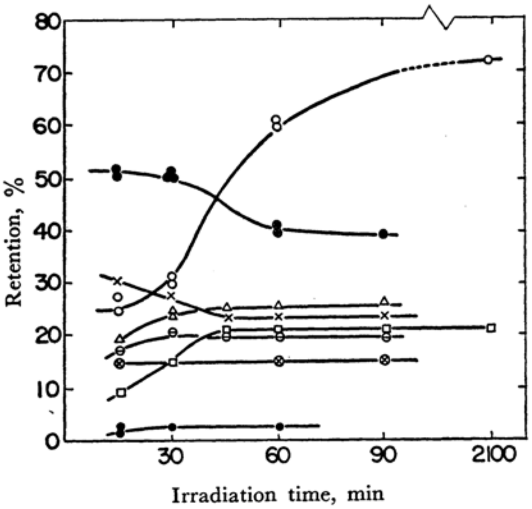


Fig. 8. Retention as a function of the irradiation time.

Thermal neutron flux: 5×10^{12} n/cm²/sec

○…$(C_6H_5)_3P$; ⊙…$(C_6H_5)_3P{=}O$;
△…$(C_6H_5O)_3P$; ×…$(CH_3C_6H_4O)_3P$;
□…$(C_6H_5O)_3P{=}O$; ⊖…$(C_6H_5O)_2POH$;
⊗…$C_6H_5OP{=}O(OH)_2$;
●…$C_6H_5P{=}O\cdot H\cdot OH$

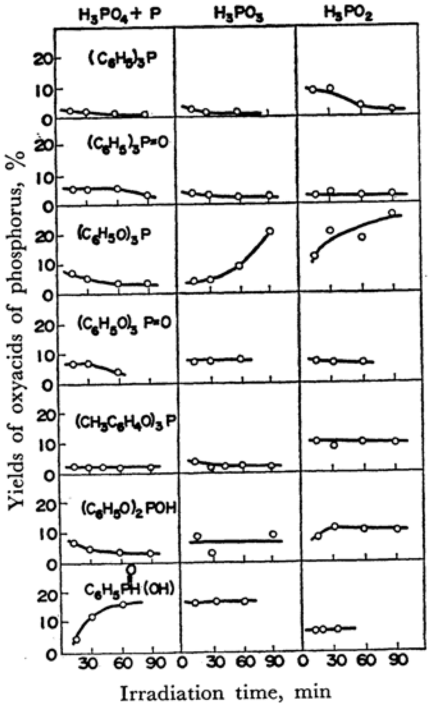


Fig. 9. Yields of ^{32}P-labeled phosphorus oxyacids as a function of the irradiation time.
Thermal neutron flux: 5×10^{12} n/cm²/sec
Irradiation time: 15—90 min

The percentage of the retention[14] of each target material is estimated from such figures as Fig. 5 and is plotted against the irradiation time in Fig. 8. At short irradiation time, the retention changes with the irradiation time, especially in triphenylphosphine. However, it reaches a constant value over 60 min. These results can also be explained by the effects of the oxygen absorbed in a sample. At this irradiation time, the retention decreases in the following order: triphenylphosphine > triphenylphosphine oxide > triphenylphosphite > tricresylphosphite > triphenylphosphate > diphenylphosphite > monophenylphosphate > phenylphosphonous acid. The retention is lower in the target material with a hydroxyl group in its molecule, and among the target materials without a hydroxyl group, it is roughly proportional to the number of oxygen atoms in the molecule.

The percentages of labeled phosphorus oxyacids, phosphoric, phosphorous and hypophosphorous acids, were estimated in a similar manner and plotted against the irradiation time for each target material (Fig. 9). The target compounds containing an oxygen atom bonded as P=O yielded more

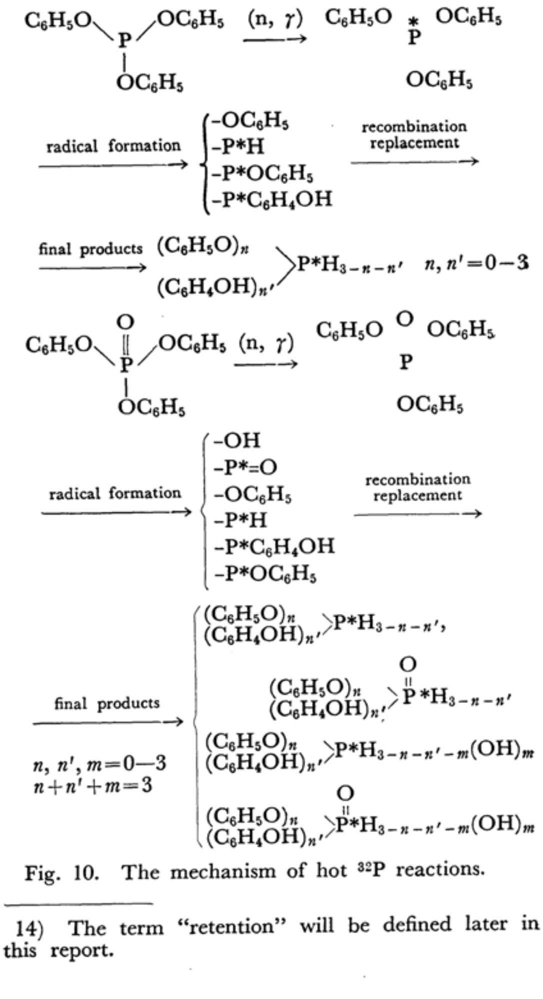


Fig. 10. The mechanism of hot ^{32}P reactions.

---

[14] The term "retention" will be defined later in this report.

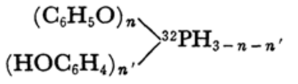
phosphoric or phosphorous acid than hypophosphorous acid. On the other hand, the compounds without an oxygen atom in the form of P=O gave more hypophosphorous acid than phosphorous or phosphoric acid. The effect of the absorbed oxygen also appeared at a short irradiation time as Fig. 9 shows.

Generally speaking, the effect of the absorbed oxygen is always observed at a short irradiation time, but it cannot be seen at a longer irradiation time, as Figs. 2, 4, 8 and 9 show.

It is also clear that the oxygen atom of the P=O group behaves differently from the oxygen atom in the form of POH or POC_6H_5 in the recoil ^{32}P reaction process (Figs. 2, 5, 6, 7, and 8).

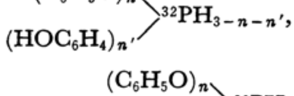
As a ^{32}P atom at birth gains a large kinetic energy by recoil upon γ-ray emission, the bond breaking occurs at the position directly bonded to the phosphorus atom. In other words, the primary retention of phosphorus compounds is negligibly small[15] and no bond-breaking between the oxygen atom and the hydrogen atom, or between the oxygen atom and the carbon atom, occurs. For example, triphenylphosphite, which has no P=O group, decomposes into a hot ^{32}P atom and three OC_6H_5 radicals in the (n, γ) reaction, as is illustrated in Fig. 10.

Hydrogen radicals, which are ejected from the target materials by the first neutrons, γ-ray, or the recoil atom, can also contribute to the chemical reaction of the ^{32}P atom. Accordingly, radicals such as OC_6H_5, ^{32}PH, $^{32}POC_6H_5$, and $^{32}PC_6H_4OH$ are produced uniformly in the system and recombine with each other to give the final products, the chemical formula of which is generally expressed by:

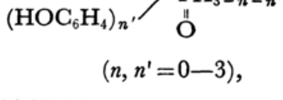


$$\left.\begin{array}{l}(C_6H_5O)_n\\(HOC_6H_4)_{n'}\end{array}\right\rangle {}^{32}PH_{3-n-n'} \quad (n, n'=0\text{—}3).$$

On the other hand, triphenylphosphate, having a P=O group, produces a ^{32}P atom, three OC_6H_5 radicals and a oxygen atom. These species and hydrogen give O, H, ^{32}PH, $^{32}POC_6H_5$, $^{32}PC_6H_4OH$, OH, and $^{32}P=O$ radicals. The chemical formulas of the final products obtained by the recombination reaction of these radicals are expressed by:

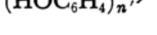


$$\left.\begin{array}{l}(C_6H_5O)_n\\(HOC_6H_4)_{n'}\end{array}\right\rangle {}^{32}PH_{3-n-n'},$$



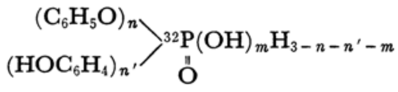
$$\left.\begin{array}{l}(C_6H_5O)_n\\(HOC_6H_4)_{n'}\end{array}\right\rangle \underset{\overset{\|}{O}}{{}^{32}P}H_{3-n-n'}$$

$$(n, n'=0\text{—}3),$$



$$\left.\begin{array}{l}(C_6H_5O)_n\\(HOC_6H_4)_{n'}\end{array}\right\rangle {}^{32}P(OH)_mH_{3-n-n'-m}$$

and



$$\left.\begin{array}{l}(C_6H_5O)_n\\(HOC_6H_4)_{n'}\end{array}\right\rangle \underset{\overset{\|}{O}}{{}^{32}P}(OH)_mH_{3-n-n'-m}$$

$$(n, n', m=1\text{—}3).$$

According to this mechanism, it seems that the recoil products with a P=O or OH group are produced only from the target materials with a P=O or OH group. This theory is in agreement with the experimental results concerning the aqueous solubility of the recoil products shown in Fig. 2. The reaction site of the OC_6H_5 radical with P is of more than two; as a result, the number of recoil products must be larger in target materials with an OC_6H_5 group.

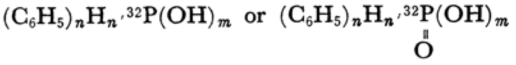
Assuming the probabilities of the formation of all the recoil products to be equal, the kinds and yields of recoil products are estimated according to the reaction mechanism described above. Although the assumption is too simple to explain all the experimental results exactly, it is permissible on the whole.

Triphenylphosphine, which decomposes into a hot ^{32}P atom and three C_6H_5 radicals in a (n, γ) reaction, gives labeled elementary phosphorus, $(C_6H_5)_3{}^{32}P$, $(C_6H_5)_2{}^{32}PH$, $C_6H_5{}^{32}PH_2$, and $^{32}PH_3$ as the final recoil products. Accordingly, the number of the products is five, and the percentage of the gaseous product, phosphine, is 20. All of the nonvolatile products are insoluble in an aqueous solution. Since the separation of $(C_6H_5)_3{}^{32}P$, $(C_6H_5)_2{}^{32}PH$, and $C_6H_5{}^{32}PH_2$ was impossible by the present paper chromatographic technique, the retention adopted here is the sum of the yields of the three compounds.

In triphenylphosphine oxide, a hot ^{32}P atom, three C_6H_5 radicals, and an oxygen atom are produced in a (n, γ) reaction; the general formulas of the recoil products are expressed by:

$$(C_6H_5)_nH_{3-n}{}^{32}P, \qquad (C_6H_5)_nH_{3-n}{}^{32}P{=}O,$$

$$(n=0\text{—}3)$$



$$(C_6H_5)_nH_{n'}{}^{32}P(OH)_m \text{ or } (C_6H_5)_nH_{n'}\underset{\overset{\|}{O}}{{}^{32}P}(OH)_m$$

$$(n, n'=0\text{—}2;\ m=1\text{—}3;\ n+n'+m=3).$$

Such recoil products as $(C_6H_5)_nH_{3-n}{}^{32}P$ or $(C_6H_5)_nH_{3-n}{}^{32}P{=}O$ ($(C_6H_5)_3{}^{32}P$, $(C_6H_5)_2H^{32}P$, $C_6H_5{}^{32}PH_2$, $^{32}PH_3$, $(C_6H_5)_3{}^{32}P{=}O$, $(C_6H_5)_2H^{32}P{=}O$, $C_6H_5{}^{32}PH_2{=}O$ and $^{32}PH_3{=}O$) and elementary phosphorous are insoluble in an aqueous solution. On the other hand, such recoil products as $(C_6H_5)_n$-$H_{n'}{}^{32}P(OH)_m$ or $(C_6H_5)_nH_{n'}{}^{32}P{=}O(OH)_m$

---

[15] a) I. G. Campbell, *Nukleonika*, **2**, 605 (1957); b) I. G. Campbell, *Polish Acad. Sci., Inst. Nucl. Res., Rept.* No 9/V (1958). c) I. G. Campbell, A. Poczynajlo and A. Siuda, *J. Inorg. Nucl. Chem.*, **10**, 225 (1959); d) M. Halmann and L. Kugel, ibid., **25**, 1343 (1963); e) A. Henglin, H. Drawe and D. Perner, *Radiochim. Acta*, **2**, 19 (1963).

TABLE 2. ESTIMATION OF RECOIL PRODUCTS

Target	Recoil products		Aqu. prod.	No. of prod.	Gas. prod., %	Aqu. ext., %	Ret. %
$(C_6H_5)P_3$	$(C_6H_5)_nH_{3-n}P \quad n=0\text{—}3$	P	no	5	20.0	0	75
$(C_6H_5)_3P{=}O$	$\left.\begin{array}{l}(C_6H_5)_nH_{3-n}P\\(C_6H_5)_nH_{3-n}P{=}O\end{array}\right\} n=0\text{—}3$	P	no	9	5.5	52.9	41.2
	$\left.\begin{array}{l}(C_6H_5)_nH_{n'}P(OH)_m\\(C_6H_5)_nH_{n'}P{=}O(OH)_m\end{array}\right\} \begin{array}{r}n, n'=0\text{—}2\\m=1\text{—}3\end{array}$		yes	9			
$(C_6H_5O)_3P$	$\left.\begin{array}{l}(C_6H_5O)_n\\(HOC_6H_4)_{n'}\end{array}\right\rangle PH_{3-n-n'}$ $n, n'=0\text{—}3$ $n+n'=3$	P	no	11	9.1	0	30
$(C_6H_5O)_3P{=}O$	$\left.\begin{array}{l}(C_6H_5O)_n\\(HOC_6H_4)_{n'}\end{array}\right\rangle PH_{3-n-n'}$ $\left.\begin{array}{l}(C_6H_5O)_n\\(HOC_6H_4)_{n'}\end{array}\right\rangle \underset{\underset{\displaystyle O}{\|}}{P}H_{3-n-n'}$ $n, n'=0\text{—}3$	P	no	21	2.6	46	16.2
	$\left.\begin{array}{l}(C_6H_5O)_n\\(HOC_6H_4)_{n'}\end{array}\right\rangle PH_{3-n-n'-m}(OH)_m$ $\left.\begin{array}{l}(C_6H_5O)_n\\(HOC_6H_4)_{n'}\end{array}\right\rangle \underset{\underset{\displaystyle O}{\|}}{P}H_{3-n-n'-m}(OH)_m$ $n, n'=0\text{—}2,\ m=1\text{—}3$		yes	17			
$C_6H_5\underset{\underset{\displaystyle O}{\|}}{P}H(OH)$	$\left.\begin{array}{l}(C_6H_5)_nH_{3-n}P\\(C_6H_5)_nH_{3-n}P{=}O\end{array}\right\} n=0\text{—}1$	P	no	5	9.1	79.1	18.2
	$\left.\begin{array}{l}(C_6H_5)_nH_{3-n-m}P(OH)_m\\(C_6H_5)_nH_{3-n-m}\underset{\underset{\displaystyle O}{\|}}{P}(OH)_m\end{array}\right\}$ $n=0\text{—}1,\ m=1\text{—}3$		yes	6			
$C_6H_5\underset{\underset{\displaystyle O}{\|}}{P}(OH)_2$	$\left.\begin{array}{l}(C_6H_5)_nH_{3-n}P\\(C_6H_5)_nH_{3-n}P{=}O\end{array}\right\} n=0\text{—}1$	P	no	5	8.3	81.8	10.9
	$(C_6H_5)_nH_{3-n-m}P(OH)_m$ $(C_6H_5)_nH_{3-n-m}\underset{\underset{\displaystyle O}{\|}}{P}(OH)_m$ $n=0\text{—}1,\ m=1\text{—}3$		yes	7			
$(C_6H_5O)_2POH$	$\left.\begin{array}{l}(C_6H_5O)_n\\(HOC_6H_4)_{n'}\end{array}\right\rangle PH_{3-n-n'}$	P	no	7	6.7	57	7.2
	$\left.\begin{array}{l}(C_6H_5O)_n\\(HOC_6H_4)_{n'}\end{array}\right\rangle PH_{3-n-n'-m}(OH)_m$ $n, n'=0\text{—}2,\ m=1\text{—}3$		yes	8			

($(C_6H_5)_2{}^{32}P(OH)$, $C_6H_5{}^{32}P(OH)_2$, $C_6H_5\cdot H^{32}P(OH)$, $(C_6H_5)_2{}^{32}P{=}O(OH)$, $C_6H_5\cdot H^{32}P{=}O(OH)$, $C_6H_5{}^{32}P{=}O(OH)_2$, $H_2{}^{32}P{=}O(OH)$, $H^{32}P{=}O(OH)_2$ and ${}^{32}P{=}O(OH)_3$) are soluble in an aqueous solution. The total number of recoil products is 18, and the percentage of phosphine is 5.5. The percentage of the aqueous extract is obtained by the equation:

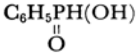
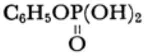
$$\frac{\text{the number of the products which are soluble in water}}{\text{the total number of products-1}^{*1}} \times 100$$

This percentage is found to be 52.9. The retention percentage is 41.2 (a mixture of $(C_6H_5)_2H^{32}P{=}O$, $(C_6H_5)_3{}^{32}P$, $(C_6H_5)_2H^{32}P$, $C_6H_5{}^{32}PH_2$, $(C_6H_5)_3$-${}^{32}P{=}O$ and $C_6H_5{}^{32}P{=}O\cdot H_2$).

For all the other target materials, the number of products, the percentage of the volatile products, the aqueous extract, and the retention were calculated in a similar manner; they are listed in Table 2.

[*1] The gaseous product is omitted in the calculation of the percentage of the aqueous extract and/or the retention.

TABLE 3. THE CALCULATED AND OBSERVED PERCENT OF RECOIL PRODUCTS

Target	Recoil product, %							
	Volatile		Aqu. ex.		Retention		Inorg. phos.	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
$(C_6H_5)_3P$	20	12.4	0	7.2	75	61	0	4
$(C_6H_5)_3P{=}O$	5.5	0	52.9	58	35.2	39	16.5	13
$(C_6H_5O)_3P$	9.1	12.2	7.5	30	30	25	0	26
$(C_6H_5O)_3P{=}O$	2.6	3.2	46	44	16.2	21	10.8	15
 $C_6H_5\underset{\underset{O}{\Vert}}{P}H(OH)$	9.1	0	45.5	79.1	18.2	16	27.3	33
$C_6H_5P{=}O(OH)_2$	8.3	0	81.7	99.1	10.9	7	27.2	
$(C_6H_5O)_2POH$	7.1	7.5	57	25.3	7.2	6	21	20
 $C_6H_5O\underset{\underset{O}{\Vert}}{P}(OH)_2$	6.2	0	86.6	99	6.7	10		

The calculated values coincide with the observed values, as is shown in Table 3. The largest yield of phosphine is observed in triphenylphosphine, as expected.

The least percentage of the aqueous extract could be expected in triphenylphosphine; this was practically established.

Differences between the calculated and observed values are mainly found in hydroxylic phosphorus compounds; they may be due to the high reactivity of the phosphorus atom for the hydroxyl group.

In conclusion, in a ^{31}P (n, γ)^{32}P reaction, a phosphorus atom in phenylphosphorus compounds breaks all the chemical bonds with which the atom binds the other atoms directly. After slowing down after collision with the surrounding molecules, the atom gives ^{32}P-labeled products. The chemical forms of the products are greatly influenced by the chemical species around the atom. A general rule for the relationship between the chemical forms of the target materials and the recoil products has been derived.