THE CHEMICAL EFFECTS OF RADIOPHOSPHORUS RECOILING FROM NUCLEAR REACTIONS

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I. NUCLEAR REACTIONS OF PHOSPHORUS

The normal chemical reactions require activation energies of less than about 50 kcal./mole. Only those reactions in which an appreciable fraction of reactant molecules can reach this energy at a temperature not very far removed from room temperature can be easily studied. It is usually not possible to carry out reactions with much higher activation energies by simply increasing the temperature of the whole reactant mixture, since many other side reactions, and particularly thermal decomposition, will compete with the desired reaction. However, atoms or ions of high energy can be obtained as recoiling particles of *nuclear* reactions. The newly formed atoms are of interest because of the unusual pathways by which they lose energy and end up in stable combination. Such hot-atom reactions are often postulated to be involved in the chemical effects of ionizing radiations. By using radioactively labeled hot atoms, their properties can be more directly studied (92). The chemical reactions of newly formed elements might also be of assistance in understanding the creation of chemical compounds in the universe (72). In the present review, the literature on recoiling radiophosphorus has been surveyed through 1963.

While normal phosphorus, P^{31}, is a stable isotope with a natural abundance of 100%, six radioactive isotopes have been prepared. These isotopes are listed in Table I together with data on their half-lives, main methods of formation, and modes of decay (107).

The only radioisotope which has found wide use is P^{32}, which has a convenient half-life and is very easily obtained by thermal neutron activation of natural phosphorus or by fast neutron activation of sulfur. Phosphorus-33 which is obtained by thermal neutron capture in the rare stable sulfur-33, would be very convenient for many tracer applications because of its longer (4 weeks) half-life. An added advantage for biological work is the lower energy of the β-emission from P^{33}. It is, however, not yet easily available in radiochemically pure form, since its production involves the separation of sulfur-33 (37, 119). Phosphorus-32 is also produced by the β-decay of silicon-32, which has a half-life of several hundred years (68, 115). Sources of Si^{32} have been prepared by the reaction $Si^{30}(t,p)Si^{32}$ based on neutron activation of lithium silicide (54). This material should be convenient as a "cow" which could be milked periodically for its daughter P^{32}.

TABLE I

RADIOISOTOPES OF PHOSPHORUS

Isotope	Half-life	Methods of formation	Modes of decay and energies of radiation, Mev.
${}_{15}P^{22}$	0.28 sec.	$Si^{28}(p,n)$	β^+ 10.6; γ 1.79
${}_{15}P^{29}$	4.5 sec.	$Si^{28}(d,n)$	
		$Si^{29}(p,n)$	β^+ 3.95; γ 1.28
		$P^{31}(\gamma,2n)$	
${}_{15}P^{30}$	2.52 min.	$P^{31}(n,2n)$	
		$S^{32}(d,\alpha)$	β^+ 3.24; γ 2.16
		$Al^{27}(\alpha,n)$	
${}_{15}P^{32}$	14.2 days	$P^{31}(n,\gamma)$; $Cl^{35}(n,\alpha)$	β^- 1.707; *no* γ
		$P^{31}(d,p)$; $S^{32}(n,p)$	
${}_{15}P^{33}$	25.2 days	$S^{33}(n,p)$; $Cl^{37}(\gamma,\alpha)$	β^- 0.238; *no* γ
		$S^{34}(\gamma,p)$; $Cl^{35}(\gamma,2p)$	
${}_{15}P^{34}$	12.5 sec.	$Cl^{35}(n,d)$; $Cl^{37}(n,\alpha)$	β^- 5.1(75%); γ 2.1
		$S^{34}(n,p)$	β^- 3.2(25%)

The reaction $P^{31}(d,p)P^{32}$ has been used to determine the excited states of P^{32}. Silver pyrophosphate was bombarded with 6-Mev. deuterons, and the energy distribution of the emitted protons was analyzed with a magnetic spectrograph. Between the ground state and 6.2 Mev., P^{32} atoms were found to have 52 discrete energy levels (91). No attempt has yet been made to correlate chemical reactivities of hot phosphorus atoms with definite energy levels.

II. THE RECOIL PROCESS, PRIMARY RETENTION, "HOT" AND "THERMAL" REACTIONS

One of the most easily studied nuclear reactions is the capture of thermal neutrons by phosphorus. The cross section for this process is quite high, 0.20 barn. The collision of a thermal neutron which has an average energy of 0.035 e.v. with a phosphorus atom does not provide enough energy to break the chemical bonds to phosphorus. However, neutron capture is followed by the emission of γ-rays. In this radiative thermal neutron capture of phosphorus, $P^{31}(n,\gamma)P^{32}$, the mass of the product nucleus P^{32} is less than the sum of the masses of the starting nuclei (P^{31} and neutron). The newly formed nucleus has excess energy, which it emits partly by a cascade of γ-rays, and which in part is converted into translational energy (and other degrees of freedom).

If all the γ-ray energy was emitted as a single quantum of γ-rays, it would be simple to calculate the energy of recoil of the newly formed P^{32} nucleus using the laws of conservation of momentum and energy. However, since the γ-rays are emitted as a cascade, such a calculation is difficult. It is the recoil energy which accounts for the special reactivity of the new "hot" phosphorus atom, and knowledge of its magnitude is thus of fundamental importance. The total γ-ray energy is 7.92 Mev.; in the γ-ray cascade, the most abundant transitions are of 6.76, 4.68, 3.26, 2.17, and 0.51 Mev. (11, 14, 42). The angular correlations of these γ-quanta have been measured (76) and have been found to be significantly anisotropic. However, it has not yet been possible to make a reliable prediction of the recoil energy owing to the partial cancellation of recoil. Calculations on the failure to bond rupture following (n,γ) activation in *alkyl halides* have been made and compared with experimental results for retention in gaseous systems (40). Estimates also have been made (17, 18, 87) on the probability of the newly formed P^{32} nucleus being unable to break any of its chemical bonds, thus causing the phenomenon usually named primary retention. This will happen when cancellation of recoil by several γ-quanta leaves the new nucleus with an energy which is less than the bond-dissociation energy. These calculations, based on random walk of the nucleus between successive γ-emissions, using the theory of Rayleigh (93), so far do not consider the anisotropy mentioned above (76).

A simple application of this theory is for the case of a partial cancellation of momenta of three equal γ-quanta with random angular correlation. In this case the probability of failure of bond rupture should be

$$P(r,l) = \frac{r^3}{6 \times l^3}$$

in which $r = \sqrt{2M_pE_{r,\min}}$ and $l = 32.7E_\gamma/n$. $M_p = 32$ is the mass of the recoiling phosphorus atom, $E_\gamma = 7.92$ Mev. is the total γ-energy radiated after neutron capture in P^{31}, and $n = 3$ is the average number of γ-quanta simultaneously emitted. The minimum recoil energy $E_{r,\min}$ of the recoiling P^{32} atom required to break one of its bonds is larger than the bond-dissociation energy D, because part of the recoil energy is lost as kinetic energy of the whole molecule (111). Therefore

$$E_{r,\min} = D(M_p + M_R)/M_R$$

in which M_R is the mass of the rest of the molecule. Calculated and observed results for the per cent primary retention are given in Table II.

TABLE II

Target	Primary retention, %		Ref.
	Calcd.	Obsd.	
$PCl_3(g)$	0.6	0.1–0.2	51
$PH_3(g)$	3.2		45
$P(CH_3)_3(g)$	0.14	0.05–0.1	45
$(n\text{-BuO})_3PO(l)$	2.4	5	19

The question whether primary retention does occur at all during thermal neutron capture in phosphorus seems still unsettled, but it certainly does not contribute to more than a fraction of a per cent of the total yield of radiophosphorus. The theory given above is based on the assumption that the three γ-quanta are emitted within a time that is short relative to the period of bond vibration (about 10^{-14} sec.). A longer delay time would prevent cancellation of recoil momenta and would require smaller primary retention.

Most of the new P^{32} nuclei recoil from their parent molecules with more than the usual chemical bond energy, 2–3 e.v. These "hot" nuclei lose their excess energy by collisions with other atoms and finally end up in a stable chemical combination in which they can be identified by various analytical techniques. From a knowledge of these products, it is possible to speculate on the mechanism of the product-forming steps. The two basic problems in such an investigation are: (a) to what extent are the chemical bonds of the recoiling nucleus broken, and (b) what are the reaction pathways by which the free recoiling nucleus is trapped into a stable product? In particular, attempts have been made to recognize the part of the reaction proceeding by high energy, or "hot" atoms, and that part occurring in the "thermal" stage. It is now generally accepted that in the first primary process of nuclear recoil, the newly formed atom sheds off several of its valence electrons. The isomeric transition of methyl bromide-Br^{80m} (4.4-hr. isomer) in the gas phase was studied in a mass spectrometer, and a spectrum of products was obtained including positive ions of bromine from Br^{+1} to Br^{+13}, with a maximum intensity for Br^{+7} (118). It is probable that similar highly ionized phosphorus-32 atoms are produced in the thermal neutron capture in phosphorus compounds. Due to the considerable experimental difficulties involved, such experiments have not been made so far.

The hot reactions of recoil atoms may be of two types: (a) those occurring in high local concentrations of free radicals, or "nests of radicals," and (b) "hot exchange," *i.e.*, direct displacement (104, 105). The following model was proposed for reaction of recoiling polyvalent atoms such as phosphorus in the liquid phase. The hot atom forms a nest of radicals around itself and after a sufficient number of random collisions, it combines with one of the radicals in the hot region. This new radical can then react with another one, or become stabilized by reaction with a scavenger such as oxygen. This second step may still be hot, or it may be in the thermal energy range. The addition of yet another radical will then nearly always take place in the thermal energy region. The reformation of bonds is therefore a stepwise reaction and does not proceed by hot exchange.

Experiments towards direct measurement of the energy of recoil by newly formed P^{32} have been made. The range of recoiling P^{32} atoms obtained by the S^{32}-(n,p)P^{32} reaction was determined (89) by fast neutron irradiation of a fine suspension of sulfur in water. The yield of P^{32} in the water was up to 75%, and the recoil range was calculated as 0.37 μ. An interesting application of this recoil range has been to use the recoil from a fine powder to separate short-lived P^{30} (2.5 min.), prepared according to the reaction $P^{31}(\gamma,n)P^{30}$, from the bulk of phosphorus. Red phosphorus suspended in tetralin was irradiated with a betatron (90), and part of the P^{30} was isolated by filtration in the liquid phase. The yield of this isotope can reach up to 20%, depending on the photon energy.

III. EXPERIMENTAL METHODS FOR THE STUDY OF THE CHEMICAL EFFECTS OF THE NUCLEAR RECOIL OF PHOSPHORUS

In the case of the relatively long-lived isotopes, P^{32} and P^{33}, the experimental facilities required for investigating the chemical forms of the products containing radiophosphorus are simple. The sources of bombarding particles may be thermal or fast neutrons from nuclear reactors, or heavy charged particles such as protons from various accelerators. The production of bombarding particles is fully described in the literature (38). In reactor irradiations, it is important to know the fluxes of fast neutrons, of thermal neutrons, and of γ-rays. The radiation damage due to the γ-rays can be determined by separate irradiations with a pure γ-source (*e.g.*, Co^{60}) and corrections made accordingly. Another approach is to minimize the effect of radiolysis. This is achieved by using for irradiations the "thermal column" of a nuclear reactor, in which a thermal neutron flux of about 10^{10} neutrons/cm.^{2} sec. may be obtained, while the fast neutron flux is only about 10^{-3} of that value, and the γ-flux only several hundred rads/min. Thermal columns normally operate at room temperature, but it is relatively easy to carry out experiments at other temperatures, for instance, at $-80°$ by immersing the sample in a dewar containing Dry Ice. If radiolysis by γ-rays and fast neutrons is of no concern, samples may be irradiated directly in the reactor in which the thermal neutron flux is about 1000 times higher. The amount of sample required depends on the neutron flux used, the time of irradiation, and the sensitivity of the radioactivity counting equipment available.

Crystalline or nonvolatile liquids may be placed in polyethylene flasks and irradiated in the presence of air. However, if air is to be excluded, the samples are sealed in quartz samples fitted with breakseals. Removal of traces of water or oxygen absorbed on the walls of ampoules is facilitated by repeatedly purging the system with helium and pumping down to as low a pressure as can be produced, but even rigorous precautions do not prevent appreciable amounts of oxygen atoms from remaining (72). Gaseous samples are irradiated in sealed ampoules in a similar manner.

A major difficulty in obtaining reproducible yields of P^{32}-labeled products is in preparing samples of defined purity. One approach is to purify the materials to be irradiated until further purification does not change the recoil results. Another method is to add various likely impurities deliberately and to extrapolate to zero impurity concentration.

It is important to realize that the number of water and oxygen molecules remaining, even after painstaking purification, is usually very much larger than the number of P^{32} atoms produced. A typical upper limit to the ratio P^{32} atoms/O_2 molecules is 10^{-5}. The number of radiochemical products formed after nuclear recoil is usually large and sometimes unexpected, and previously unknown compounds are obtained. Whenever possible, highly efficient methods of product separation should be used such as gas–liquid chromatography, paper chromatography, or electrophoresis, or countercurrent liquid extraction. One of the advantages of such chromatographic methods is their efficient performance even with unweighable amounts of material. The radioactivity spectrum of the chromatogram by any of these processes will indicate a number of radioactive products. Most of these can then be identified on a trial-and-error basis by using synthetic compounds and comparing their rate of movement under identical conditions (*e.g.*, retention time or R_f). These results are usually expressed as the per cent of radioactivity in a certain product compared to the total radioactivity.

One of the experimental criteria for identifying thermal reactions is the effect of changes in temperature during irradiation on the yield of reaction products.

Temperature changes usually do not affect hot reactions, while they profoundly influence thermal reactions. Another more generally useful criterion is the effect of addition of small amounts of free-radical scavengers to the system. The part of the reaction thus prevented from occurring is considered to be due to radical mechanisms in a thermal (or close to thermal) energy range. The part of the reaction which is unaffected by these scavengers is then considered to be due to hot atoms. The difficulty in studying any new system is in finding out which substances can act as radical scavengers. Thermal reactions also may be reproduced sometimes by ionizing radiations where the problems associated with nuclear recoil do not exist. The yields of hot reaction products are decreased by addition of large amounts of moderators such as inert gases, and this provides a powerful criterion for hot reactions (34, 121).

IV. RECOILING RADIOPHOSPHORUS IN ORGANIC SYSTEMS

A. ORGANIC PHOSPHORUS COMPOUNDS

The first study of the chemical effect of P^{32} produced by the (n,γ) reaction was in an organic phosphorus compound (32). Triphenyl phosphate in benzene solution was irradiated with thermal neutrons from a radium–beryllium source. About 30% of the P^{32} was produced in a form which could be absorbed by charcoal, while 40% could be extracted with water. This was thus an early application of the Szilard–Chalmers reaction to the preparation of an almost "carrier-free" isotope.

The conditions for such enrichment of the radioisotope are that P^{32} in inorganic ionic form does not exchange with the bulk of the organic phosphate (120) and that radiation damage is small.

The same reaction has again been studied with triphenylphosphine (64) and triphenylphosphine oxide (84). The reactor irradiation of tri-*n*-butyl phosphate has also been used for production of P^{32} (65, 66) or for the simultaneous production of Si^{31} and P^{32} (53). In all these investigations, no attempts were made to identify the organic P^{32}-labeled products.

The organic products containing P^{32}, formed from sulfur by the S^{32}(n,p) reaction, were studied by neutron irradiation of carbon disulfide mixtures with benzene or chlorobenzene (85, 112). Most of the activity appeared as orthophosphate and as phenylphosphonic acid, $PhPO(OH)_2$, with smaller amounts as diphenylphosphonic acid, Ph_2POOH, and triphenylphosphine, Ph_3P (see Table III). The yield of P^{32} as phenylphosphonic acid increased with increasing dilution of the carbon disulfide by the aromatic solvent. In a solvent containing mainly carbon disulfide, the recoiling radiophosphorus atom probably reacts to form unstable compounds, which on subsequent, aqueous extraction decompose to orthophosphate. In a predominantly

TABLE III

CHEMICAL PRODUCTS OF THE NUCLEAR RECOIL OF P^{32} IN ORGANIC COMPOUNDS

Nuclear reaction	Target: Compound	Target: Phase	Target: Solvent (mole %)	Flux, neutrons/ cm.² sec.	Sepn. method	Products (yield, %)	Ref.
S^{32}(n,p)	CS_2	Solution	C_6H_6 (35)	2 × 10^7	Pptn. and extn.	PO_4^{-3} (73); $PhPO_3H_2$ (25); Ph_2POOH (0.6); Ph_3P (1.7)	85
	CS_2	Solution	C_6H_5Cl (32)	2 × 10^7	Pptn. and extn.	(68) (30) (0.3) (1.4)	85
Cl^{35}(n,α)	CCl_4	Solution	C_6H_6 (46)	2 × 10^7	Pptn. and extn.	(30.2)	85
	CCl_4	Solution	C_6H_5Cl (52)	2 × 10^7		(37.7)	85
P^{31}(n,γ)	Me_3P (14 mm.)	Gas		2 × 10^{10}	Gas chrom.	PH_3 (30); $MePH_2$ (3); Me_2PH (2); Me_3P (0.6)	45
					Paper chrom. and electrophor.	PO_4^{-3} (14); HPO_3^{-2} (6); $H_2PO_2^{-2}$ (12) $MeHPO_2H$ (12); $MePO_3H_2$ (9); Me_2POOH (9)	
	Ph_3P (air)	Solid			Liquid extn. and pptn.	Aqueous extract (3)	64
	Ph_3P (vacuum)	Solid		2 × 10^{11}	Liquid extn. and pptn.	Ph_3P (2)	44
	Ph_3PO	Solid			Liquid extn. and pptn.	Aqueous extract from $CHCl_3$ (86)	84
					Co-pptn. with $Fe(OH)_3$	Adsorbed on $Fe(OH)_3$ (70)	
	n-$BuOPO_3H_2$ (air)	Liquid		10^{11}	Liquid extn. and pptn.	$(BuO)_3PO$ (2–5); $(BuO)_2PO_3H_2$ (2–3); $BuOPO_3H_2$ (26); P-inorg. (65)	105
	(*n*-$BuO)_2PO_2H$ (air)	Liquid		10^{11}	Liquid extn. and pptn.	$(BuO)_3PO$ (4); $(BuO)_2PO_3H_2$ (8); $BuOPO_3H_2$ (48); P-inorg. (22)	105
	(*n*-$BuO)_3PO$ (air)	Liquid		10^{11}	Liquid extn. and pptn.	$(BuO)_3PO$ (6.5); $(BuO)_2PO_3H_2$ (29); $BuOPO_3H_2$ (34); P-inorg. (26)	105
	(*n*-$BuO)_3PO$ (+I_2)	Liquid		2.6 × 10^{11}	Liquid extn. and pptn.	$(BuO)_3PO$ (5.0); $(BuO)_2PO_3H_2$ (19); $BuOPO_3H_2$ (41); P-inorg. (30)	105
	(*n*-$BuO)_3PO$ (vacuum)	Liquid		2.6 × 10^{11}	Liquid extn. and pptn.	$(BuO)_3PO$ (21); $(BuO)_2PO_3H_2$ (27); $BuOPO_3H_2$ (30); P-inorg. (19)	105
	(*n*-$BuO)_3PO$ (air)	Solid (−80°)		2.6 × 10^{11}	Liquid extn. and pptn.	$(BuO)_3PO$ (11); $(BuO)_2PO_3H_2$ (57); $BuOPO_3H_2$ (28); P-inorg. (19)	105
	(*n*-$BuO)_3PO$ (air)	Liquid		10^7	Extn. with KOH (pH 12.5)	Aqueous extract (54)	53
	$(PhO)_3PO$	Solution (C_6H_6)			Liquid extn.	Aqueous extract (40); adsorbed on charcoal (30)	32
	H_3PO_4	Solution (glycerol)		10^{12}	Paper chrom.	H_3PO_3 (19); H_3PO_2 (11); glycerophosphorus acid (9)	122

aromatic solvent, stable phenylphosphorus bonds are formed.

A systematic study of P^{32} recoil in an organic phosphate was the investigation of the neutron activation of liquid tri-*n*-butyl phosphate (19). At a high neutron flux in the reactor (10^{12} neutrons/cm.^{2} sec.), about 60% of the activity appeared in the tri-*n*-butyl phosphate fractions, while under thermal column conditions (10^9 neutron/cm.^{2} sec.), the yield of the parent fraction $(BuO_3)PO$ was reduced to about 5% (see Table III). However, estimates based on random walk of the newly formed P^{32} between successive γ-quanta indicate that only 2 to 3% of the total amount of P^{32} could be due to primary retention, *i.e.*, in which the recoiling nucleus does not break its chemical bonds. Other products of this reaction were mainly orthophosphoric and phosphorous acids and mono- and di-*n*-butylphosphoric acids.

In order to gain further information on the extent of primary retention by recoiling P^{32}, the irradiation of gaseous trimethylphosphine by thermal neutrons was investigated (43–46, 62, 63). Gas chromatography was used for the separation of the volatile products. Under thermal column conditions, almost all the volatile activity appeared as phosphine, and only about 1% was isolated as the parent compound. A few per cent of the volatile activity was also found as mono- and dimethylphosphines. The yield of phosphine formed dropped as the neutron and γ-flux was raised, probably due to radiation decomposition. From a study of the dependence of the yield of trimethylphosphine-P^{32}, on (a) variation of the pressure of irradiated trimethylphosphine and (b) the effect of added argon gas, it was concluded that the parent yield is essentially due to recombination reactions of hot P^{32} atoms. The primary retention in gaseous trimethylphosphine must be less than 0.05% of the total radiochemical yield. The nonvolatile products deposited on the walls of the ampoules after neutron irradiation of gaseous trimethylphosphine were separated by paper chromatography and electrophoresis and identified as inorganic and methyl-substituted derivatives of phosphorus oxyacids. In solid triphenylphosphine (44), thermal neutron irradiation yielded P^{32} activity both in inorganic oxyacids of phosphorus and phenyl-substituted phosphorus compounds. The products were separated by liquid extraction, yielding about 2% of the activity as triphenylphosphine. The yield of triphenylphosphine obtained in these experiments was similar to that obtained by the neutron activation of carbon disulfide in benzene (85). It is therefore unlikely that the 2% parent yield after neutron irradiation of triphenylphosphine is a primary retention.

The special features of the recoil chemistry of multivalent atoms such as phosphorus and arsenic have been considered (104–106). During recoil, each bond may break in succession. Similarly, the formation of stable chemical bonds may take place in one or several stages. These steps may occur while the atom is still hot, or when it has slowed down to the thermal energy range. After neutron irradiation of tri-*n*-butyl phosphate *in vacuo* (see Table III), 21% of the activity appeared as the starting material, while in the presence of added free-radical scavengers, such as air, oxygen, or iodine, the parent yield dropped to 6%. In this case 15% of the total yield is considered to be due to a thermal reaction of free radicals. In the remaining 6%, the contribution from hot reactions was determined by separate irradiations of di-*n*-butyl hydrogen phosphate and *n*-butyl dihydrogen phosphate with neutrons, using air as a scavenger. Here the tri-*n*-butyl derivative in the product obviously cannot be formed either by survival of the bonds or by thermal reactions. Its yield from these acids was 2–4%, and this must be deducted from the 6%, to give an upper value of 2–4% for the primary retention for tri-*n*-butyl phosphate.

The result from all these investigations is that primary retention does not play an important role in the formation of the products. Hot reactions were found to be dominant in the formation of *n*-butyl dihydrogen phosphate and di-*n*-butyl hydrogen phosphate from tri-*n*-butyl phosphate, since their yield (30 and 27%) was unchanged on the addition of scavengers.

B. PHOSPHORUS TRICHLORIDE IN ORGANIC SOLVENTS

The radiative thermal neutron capture in solutions of phosphorus trichloride has been studied (50, 51). In mixtures of phosphorus trichlorides with carbon tetrachloride, the observed retention (activity recovered as PCl_3) was about 65%, just as in pure phosphorus trichloride. In hydrocarbon solutions, the observed retention dropped with increasing dilution. The effect was most pronounced with cyclohexene, which is known from radiation chemistry studies to be a very good scavenger for free chlorine atoms and molecules. At high dilutions of phosphorus trichloride with cyclohexene, the retention reached a limiting value of about 6%, which was considered by the authors to be due to neutron capture processes in which the phosphorus–chloride bonds of PCl_3 were not broken. It should, however, be recalled that solutions of phosphorus trichloride in hydrocarbons are not ideal and that phosphorus trichloride molecules are probably aggregated to dimers and larger clusters. Even in dilute solutions, the neutron-capture process may create "cages" of hot phosphorus and chlorine atoms which can recombine and reform the parent compound.

In the gas phase too, the observed retention of P^{32} in phosphorus trichloride is strongly decreased by addition of hydrocarbon vapors (30). Thus in a mixture of 3 volume % phosphorus trichloride and 97% cyclohexene in the gas phase, the retention reaches a limiting value of 0.1 to 0.2%. This observed retention is, however, lower than that predicted by the "random walk theory" (17, 18) mentioned in the previous section. By this theory, assuming the radiative neutron capture of phosphorus to yield three equal γ-quanta per cascade of $7.92/3 = 2.64$ Mev., the primary retention should be 0.6%.

The observed retention of P^{32} as $P^{32}Cl_3$ after neutron activation of gaseous phosphorus trichloride was *partly* due to hot recoil atoms (47%), which could be inhibited by argon and other moderators at high concentrations, and *partly* due to rechlorination of thermal phosphorus atoms (28%), which could be inhibited by small amounts of hydrocarbon scavengers of chlorine atoms (51).

C. PHOSPHORUS COMPOUNDS OF BIOLOGICAL INTEREST

Neutron activation of crystalline nucleotides such as adenosine triphosphate yielded products in which no gross decomposition could be detected by physical or biological means (77). However, extensive local decomposition in the vicinity of the recoiling P^{32} atoms was proven by the noncorrespondence of ultraviolet-absorbing spots and radioactivity after paper chromatography of irradiation products. The parent yields were less than 1% in these nucleotides (78).

A further application of recoil labeling of a complex organic phosphate was the neutron activation of crystalline deoxyribonucleic acid (DNA) (47). Crystalline DNA, containing 20–30% of water was irradiated with thermal neutrons, either for a few minutes in a pneumatic tube (10^{12} neutrons/cm.^{2} sec.), or for about 4 days in a thermal column (10^{10} neutrons/cm.^{2} sec.). In either case the extent of radiolytic damage, measured by the macroscopic physical properties (viscosity, sedimentation constant, and hyperchromicity) after dissolution of the irradiated DNA, was moderate. However, examination of the distribution of P^{32} activity indicated that 50 ± 10% of the radiophosphorus had been ejected from the long-chain molecule and could be removed by dialysis. Paper chromatography showed that it contained mainly inorganic phosphorus oxyacids. The remaining 50% of P^{32} was not in the form of phosphate end groups (primary phosphate esters), because no appreciable additional P^{32} activity was liberated from the irradiated DNA by incubation with alkaline phosphatase. This fraction of P^{32}, presumably in high molecular weight combination, was, however, not in the form of intact sugar phosphate bonds of normal DNA, because treatment with desoxyribonuclease followed by alkaline phosphatase did not liberate the P^{32} as orthophosphate, although it did hydrolyze the bulk of the irradiated DNA (48).

Neutron irradiation of phosphorus oxyacids in glycerol (122) produced P^{32}-labeled phosphorous and hypophosphorous acids as well as glycerophosphorous acid. Thus, in a reducing medium like glycerol, the recoiling P^{32}, after loosing its excess energy, ends up in a state less oxidized than it would in water, in which 99% of the activity was observed in the orthophosphate fractions (96–98).

V. RECOILING RADIOPHOSPHORUS IN INORGANIC PHOSPHORUS COMPOUNDS

A. PHOSPHORUS OXYACIDS

The general principles of the effects of nuclear recoil in the solid phase have been extensively reviewed and related to theories of solid-state physics (12, 49) and will only briefly be discussed here. The pioneering work on the effects of thermal neutron capture on inorganic phosphates was carried out by Libby (67). He found that after neutron irradiation of aqueous solutions of phosphoric acid or phosphates at various pH, or of crystals of $NaH_2PO_4 \cdot H_2O$, $Na_2HPO_4 \cdot 12H_2O$, and $Na_3PO_4 \cdot 12H_2O$, the yield of orthophosphate was always about 50%, while the other 50% was transformed into a form which he collected together with a phosphite carrier. Libby concluded that about half the recoils of the phosphorus nuclei cause ejection of an unchanged oxygen atom, leaving a tervalent phosphorus atom. The amount of retention is determined by the initial recoil. He found that in the (n,γ) reaction on crystalline sodium phosphite, $Na_2HPO_3 \cdot 5H_2O$, the radiochemical yield as phosphite was 92%, while only 8% was converted into phosphate. There was thus no appreciable increase in the oxidation number of phosphorus in the case of solid phosphite.

Libby's study of the neutron activation of inorganic phosphorus oxyacids and salts has been repeated under a variety of conditions, and using several analytical techniques (13, 35, 73, 74, 96–100, 113). It was observed (96–100) that after reactor irradiation of orthophosphoric acid, pyrophosphoric acid, trimetaphosphoric acid, and their salts, virtually all the radioactivity was observed in the parent species. This was explained as being due to the great chemical stability of the phosphorus–oxygen bonds, which enabled the dissemination of the nuclear recoil energy without breaking the chemical bonds to phosphorus (primary retention). In phosphine, as well as in phosphorus oxyacids containing P–H bonds, neutron irradiation caused the formation of various decomposition products (see Table IV).

The above results may, however, also be understood as an effect of heat or radiation annealing. The concept of annealing has been applied by solid-state physicists to describe removal of local disturbances in crystals.

After neutron irradiation of various crystalline inorganic phosphorus compounds under conditions of

TABLE IV

CHEMICAL PRODUCTS OF RECOILING P^{32} IN ACIDS AND SALTS OF PHOSPHORUS OXYACIDS[a]

Compound	Flux, neutrons/cm.^{2} sec.	Sepn. method[b]	Yield of products,[c] %								Ref.
			$H_2PO_2^-$	$H_2PO_3^-$	$H_2PO_4^-$	$H_2P_2O_7^{-2}$	$\overset{5}{P}-O-\overset{3}{P}$	$\overset{4}{P}-\overset{4}{P}$	$\overset{4}{P}-\overset{2}{P}$	$\overset{5}{P}-O-\overset{5}{P}-O-\overset{5}{P}$	
a. Liquids											
H_3PO_4 (air)	4×10^{11}	PC	← 5.1 →		89	2.5	⟵	2.0	⟶		123
H_3PO_4 (vac.; liq.)	8×10^{11}	PE			~90						96
b. Solids											
Na_2HPO_4 (vac.)	1×10^{13}	PE			~90						96
Na_2HPO_4	2×10^{12}	PE	10.6	12.4	9.9	13.5	24.3	1.0	6.3	11.1	70
Na_2HPO_4 (air)	5×10^{11}	PC	← 17 →		21	26	⟵	16	⟶		123
NaH_2PO_4	2×10^{12}	PE	8.1	16.1	18.6	13.7	18.3	1.4	5.3	8.2	70
NaH_2PO_4 (air)	2.2×10^{11}	PC	← 4.7 →		79	9	⟵	8	⟶		123
KH_2PO_4	2×10^{12}	PE	8.0	11.4	10.9	15.8	21.6	1.0	2.8	13.4	70
KH_2PO_4 (air)	2.2×10^{12}	PC	← 14 →		43	12	⟵	10	⟶		123
$NH_4H_2PO_4$	2×10^{12}	PE	8.4	14.3	9.6	16.3	17.3	1.0	2.7	11.2	70
$NH_4H_2PO_4$ (air)	0.51×10^{12}	PC	← 13 →		48	8	⟵	30	⟶		123
Na_2HPO_4 (vac.)	10^{13}	PE			~100						100
Na_2HPO_4	2×10^{12}	PE	10.4	10.1	9.7	10.6	25.5	2.4	9.9	10.5	70
Na_2HPO_4 (air)	4.8×10^{11}	PC	← 20 →		24	17	⟵	37	⟶		123
K_3PO_4	2×10^{12}	PE	6.0	11.5	18.2	9	22	6	16	5	70
$(NH_4)_3PO_4$	2×10^{12}	PE	16	23	19				3.5		70
Li_3PO_4	2×10^{12}	PE	3.3	5.4	30	6	23	2.8	8		70
Na_3PO_4 (air)	4.8×10^{12}	PC	← 24.2 →		20.7	18	⟵	35	⟶		123
$Na_3PO_4 \cdot 12H_2O$	2×10^{12}	PE	10	23	37	13	9	2	2	1	70
$Na_3PO_4 \cdot 12H_2O$ (air)	4.8×10^{11}	PC	← 4.7 →		46		⟵	7	⟶		123
Na_2HPO_3 (vac.)	10^{13}	PE			~100						100
$Na_2HPO_3 \cdot 5H_2O$	2×10^{12}	PE	23.6	34.4	3.7	3.8	5.3	4.5			70
$Na_2HPO_3 \cdot 5H_2O$	4.8×10^{11}	PC	← 77 →		4.5	10	⟵	8	⟶		123
$Na_4P_2O_7$ (vac.)	1×10^{13}	PE				~90					96
$Na_4P_2O_7$ (air)	2×10^{12}	PE	4.6	12.2	8.2	6.2	12	1.6			70
$Na_4P_2O_7$ (air)	3.8×10^{12}	PC	← 26 →		9	36	⟵	26	⟶		123
$Na_4P_2O_7 \cdot 10H_2O$	2×10^{12}	PE	11.7	28.4	29.2[d]	4.4	6.3				70
$Na_4P_2O_7 \cdot 10H_2O$ (air)	4.8×10^{12}	PC	← . . . →		48	45	⟵	7	⟶		123
NaH_2PO_2 (vac.)	1×10^{13}	PE	62.0	20.0	2.0						100
$NaH_2PO_2 \cdot H_2O$	2×10^{12}	PE	42.1	22.4	6.8	1.5	2.5	2.4			70
$Na_2H_2P_2O_7$	4.8×10^{11}	PC			26						103

[a] Nuclear reaction $P^{31}(n, \gamma) P^{32}$. [b] PC = paper chromatography, PE = paper electrophoresis. [c] $\overset{5}{P}-O-\overset{3}{P}$ is $(HO)_2P(O)-O-P(O)(H)OH$; $\overset{4}{P}-\overset{4}{P}$ is $(HO)_2P(O)-P(O)(OH)_2$; $\overset{5}{P}-O-\overset{5}{P}-O-\overset{5}{P}$ is $(HO)_2P(O)-O-P(O)(OH)-O-P(O)(OH)_2$ (Blaser, 1959). [d] Includes $\overset{4}{P}-\overset{4}{P}$ fraction.

limited radiation and thermal annealing, a large number of products could be detected by paper electrophoresis (4, 70) and by paper chromatography (8, 9, 123). These include oxyanions of phosphorus containing one, two, or three phosphorus atoms. The results show that the upper limit for non-bond-rupture in inorganic phosphates is 10%. By heat or radiation annealing, the yield of the orthophosphate fraction could be increased, and results similar to those reported (96–98, 100) were obtained. Neutron activation of condensed phosphates, such as sodium trimetaphosphate (cyclic polymer) and sodium tripolyphosphate (linear-chain polymer), resulted in both degraded and polymerized recoil products (103). Some of the observed retention must have been due to thermal annealing.

A discussion of the complex results obtained by various investigators has been reviewed by Anselmo (4).

Since all methods for determining the yields of P^{32}-labeled recoil products depend on dissolution of samples after irradiation, it is interesting to find out to what extent the distribution, finally observed, already existed in the crystal. The observation of the formation of hypophosphate,$^{-2}$ $O_3P-PO_3^{-2}$, after neutron capture in KH_2PO_4 seems to prove the direct reaction of recoiling P^{32} with its environment (24). Photochemical annealing (22–24) in neutron-irradiated phosphates has been carefully studied, using both precipitation and paper electrophoretic separation techniques. The results indicate a large increase in the parent fraction after electron bombardment, ultraviolet light irradiation, or thermal annealing. The most striking observation was that the 5890-Å. line from a sodium vapor lamp did not influence the orthophosphate retention, in contrast to the effect of ultraviolet light. The threshold for photolytic annealing was found between 3000 and 2540 Å., or 4.1 and 4.9 e.v., which is the region of electronic excitation of many simple phosphorus compounds.

Thermal annealing after neutron activation of various phosphates was shown to involve both rupture of P–O–P bridges and oxidation reactions. Transformation of pyrophosphate to orthophosphate requires annealing temperatures above 100° and was suggested to be due to oxide ions. Oxidation processes, presumably by lattice defects, cause transformation of hypophosphite to phosphite, and of phosphite to polyphosphate. Annealing by ultraviolet radiation causes transformation of phosphite activity into hypophosphite. Thus hypophosphite seems to react photolytically with orthophosphate to form hypophosphate (24). Support for this hypothesis comes from a study of the electron spin resonance spectrum of γ-irradiated crystals of ammonium hypophosphite, in which the radical $H\dot{P}O_2^-$ reacts with an adjacent $H_2PO_2^-$ ion to form the radical ion $O_2P{-}PHO_2^-$ (80). Thermal annealing of recoil damage must involve different mechanisms. The activation energy distribution can be determined using Vand's concept (49, 116). The initial distribution of activation energies for thermal annealing of the polyphosphate fraction in irradiated orthophosphates was in the range of 0.60 to 1.0 e.v. (9).

In addition to annealing of the recoil damage in neutron-irradiated crystalline phosphates by thermal treatment or ultraviolet irradiation, annealing was also affected by compression. Thus Andersen (2, 3) found that pile-irradiated ammonium dihydrogen phosphate by compression to pressures of 2000 atm. had considerably increased retention (or yield as orthophosphate). Paper electrophoretic analysis of the composition of the P^{32}-labeled products before and after compression annealing showed that the major process was rupture of the P–O–P bridges. The compression annealing is thus similar to that by application of heat which was shown (24) to involve mainly the transformation of polyphosphates into orthophosphate.

B. PHOSPHORUS HALIDES

The thermal neutron capture of phosphorus in phosphorus trichloride (28, 102) and in phosphoryl chloride (25, 26) resulted in a large fraction of the P^{32} appearing as the parent compound (88% for liquid PCl_3, for instance) (see Table V). This occurred even for the neutron irradiation of samples of gaseous phosphorus trichloride at the vapor pressure of the liquid at room temperature. The authors concluded that this may indicate the failure of bond breaking by the recoiling P^{32} atom. However, in such a highly reactive system, the probability of recombination reactions should be very high. A more reliable measure of primary retention in phosphorus trichloride was obtained by studies in its mixtures with organic diluents (51), which were discussed in the previous section on recoiling radiophosphorus in organic systems.

C. ELEMENTARY PHOSPHORUS

Neutron irradiation of white phosphorus (21) yields about 66% of the P^{32} activity in the form of red phosphorus. Annealing by heat or γ-irradiation caused further increase by a few per cent in this yield. The kinetics of the thermal annealing of the P^{32} activity from the white to the red modification was found to follow monomolecular kinetics. Cifka (21) considered the question of whether the transformation from white to red phosphorus was due to temperature increase at the point of the nuclear reaction or by ionization. The average recoil energy of P^{32} after thermal neutron capture in P^{31} is about 650 e.v. Calculations (101) show

TABLE V

CHEMICAL PRODUCTS OF RECOILING P^{32} IN RED PHOSPHORUS, WHITE PHOSPHORUS, PHOSPHORUS CHLORIDES, AND SULFUR MONOCHLORIDE

Target						
Compound	Phase	Temp., °C.	Flux, neutrons/cm.^{2} sec.	Sepn. method	P^{32} products (yield, %)	Ref.
P (red) (in presence of air)	Solid		10^{11-12}	Water extn. and paper chrom.	PO_4^{-3} (2–7); HPO_3^{-2} (51–76); $H_2PO_2^-$ (3–43)	110
P_4 (white)		−80		Liquid extn.	Red P (65–80)	21
PCl_3	Liquid	50	1–6 × 10^{11}	Fract. distn.	PCl_3 (62–95); $PSCl_3$ (1–2); high boiling products (1–29)	28 102
PCl_3	Liquid				PCl_3 (65)	50, 51
PBr_3	Liquid			Fract. distn.	PBr_3 (99 ± 2)	28
$POCl_3$ (vac.)	Liquid		6 × 10^{11} (30 sec.)	Fract. distn.	PCl_3 (57); $POCl_3$ (30); high boiling components (6)	26
$POCl_3$ (+ 1.4% PCl_3)	Liquid		6 × 10^{11} (4 min.)		PCl_3 (80); $POCl_3$ (15); high boiling components (2)	26
$PSCl_3$						25
S_2Cl_2	Liquid				PCl_3 (4); $POCl_3$ (67–76); $PSCl_3$ (4–9); distn. residue (12–20)	28
S_2Cl_2	Liquid				$PSCl_3$ (mainly)	58

that this kinetic energy should not be sufficient for self-ionization, and therefore the hot zone at the point of the nuclear reaction must be responsible for the breakage of the P–P bonds of white phosphorus (P_4) and its transformation into the polymeric red phosphorus.

The chemical forms of P^{32} after neutron irradiation of red phosphorus were also studied (110). Irradiation in the presence of air causes rupture of the P–P bonds of the red phosphorus polymer. Air oxidation yields products which can be extracted by water and identified by paper chromatography as orthophosphate, hypophosphite, and orthophosphite (see Table V).

D. PHOSPHINE

Neutron irradiation of gaseous phosphine, both in the presence of an excess of various inert gases or methane which could act as moderators for hot atoms, or in the presence of small amounts of substances which could possibly scavenge thermal phosphorus atoms, always resulted in 40 to 60% of the P^{32} to be retained as $P^{32}H_3$, while the balance was deposited on the walls as phosphorus oxyacids (46). This surprising result may be explained by the absence of hot reactions and by phosphine itself being a more efficient scavenger of thermal phosphorus atoms than other substances which were added.

VI. PHOSPHORUS OBTAINED BY NEUTRON IRRADIATION OF INORGANIC SULFUR AND CHLORINE COMPOUNDS

A. SULFUR COMPOUNDS

The first application of the $S^{32}(n,p)P^{32}$ reaction was to prepare "carrier-free" radiophosphorus containing a very high specific activity of the isotope. (The term "carrier-free" radiophosphorus means that the amount of normal phosphorus P^{31} is less than can be detected by any known method.) Some P^{31} is, however, always contained as an impurity in the sulfur. In a number of experiments carbon disulfide was irradiated with fast neutrons (33, 41, 52. 59, 75). All the P^{32} activity went along with a precipitate of red phosphorus which was formed but could be extracted from it by water. An alternative method for preparing very highly active P^{32} has been the pile irradiation of elementary sulfur (5, 10, 27, 29, 31, 39, 55–57, 60, 61, 71, 79, 86, 88, 94, 95, 117).

The production of both P^{32} and P^{33} by the pile irradiation of sulfur, according to the reaction $S^{32}(n,p)$-P^{32} with fast neutrons, and by the reaction $S^{33}(n,p)P^{33}$ with thermal neutrons, was also studied. The isotopes of phosphorus (86) were found to follow the insoluble S_μ fraction of sulfur on dissolution in carbon disulfide. This provided a convenient method of separation from the S^{35} formed simultaneously.

These preparative procedures do not provide much information on the mechanisms of reaction of the newly formed recoiling P^{32} atom.

The reaction of P^{32} produced by fast neutrons on salts of oxyacids of sulfur was first studied by Aten (6, 7). From crystalline potassium or sodium sulfates, most of the radiophosphorus appeared as orthophosphate, and only a few per cent occurred as phosphite and hypophosphite (see Table VI). On the other hand, crystalline sodium sulfite, $Na_2SO_3 \cdot 7H_2O$, yielded only about 50% as orthophosphate. From solid sodium sulfide, $Na_2S \cdot nH_2O$, less than 35% of the activity appeared as orthophosphate.

After bombardment of crystalline sulfates with fast neutrons (36), the P^{32} was found mainly as orthophosphate. However, after the irradiation of solutions of sulfates or sulfuric acid, the P^{32} formed was about equally distributed between the phosphate, phosphite, and hypophosphite ions.

A study was made (69) of the neutron activation of a number of inorganic sulfur and chlorine compounds containing hydrogen bound is various ways. All the anhydrous nonhydrogen-containing sulfates yielded P^{32} mainly as orthophosphate, while hydrates yielded appreciable (10 to 40%) yields of reduced forms of phosphorus (see Table VI). This may be due to stabilization of reduced forms of phosphorus by hydrogen, as a result of formation of P–H bonds.

Of special interest was Lindner's observation (69) that when calcium sulfide, after neutron activation, is dissolved in water, a considerable percentage of phosphine is formed. In contrast, no phosphine was found after a similar experiment with anhydrous potassium sulfide. He explained this as being due to the higher stability of calcium phosphide.

From a number of neutron-irradiation experiments on aqueous solutions of inorganic sulfur or chlorine compounds, Lindner concluded that the P^{32} formed appears in an oxidation state, which is determined by its chemical reactions with the water molecules after it has lost most of its kinetic energy. Thus the oxidation state in solution does not depend on the initial chemical form of the target atom nor on the initial recoil energy.

By the neutron irradiation of a number of inorganic salts, sulfates, and sulfites, at liquid air temperatures, Lindner studied the effect of post-irradiation annealing, the change in distribution of P^{32} between ortho- and non-orthophosphate depending on heat treatment after neutron activation. In most cases, the yield of non-orthophosphate measured, immediately after irradiation at liquid air temperature, was considerably higher than that after room temperature irradiation. Thus for anhydrous sodium sulfate, it was 12.5% compared with 7% at room temperature irradiation, but when the sample after neutron activation at liquid air temperature was left for 2 days at room temperature, its non-orthophosphate content had dropped from 12.5 to

TABLE VI
CHEMICAL PRODUCTS OF RECOILING P^{32} IN INORGANIC SULFUR COMPOUNDS[a]

Target				
Compound	Temp., °C.	Neutron source	Yield of non-orthophosphate fraction,[b] %	Ref.
a. Solids				
Li_2SO_4	30	Cyclotron	6.9	69
$Li_2SO_4 \cdot H_2O$	30	Cyclotron	20	69
$Li_2SO_4 \cdot D_2O$	30	Cyclotron	31	69
Na_2SO_4	30	Reactor	2	1
Na_2SO_4		Ra–Be source	5	58
$Na_2SO_4 \cdot 10H_2O$	30	Ra–Be source	0	
$Na_2SO_4 \cdot 10H_2O$	30		2	6, 7
$Na_2SO_4 \cdot 10H_2O$	30	Cyclotron	2.5	69
$NaHSO_4 \cdot H_2O$	30	Cyclotron	17	69
$K_2S_2O_7$ (fused)	40	Cyclotron	12.9	69
K_2SO_4	<30		10	67
K_2SO_4	<30	Cyclotron	6	69
$KHSO_4$			14	69
$(NH_4)_2SO_4$			23	69
NH_4HSO_4			25	69
$H_2NNH_2 \cdot H_2SO_4$			50	69
$2NH_2OH \cdot H_2SO_4$			18	69
$MgSO_4$			9	69
$MgSO_4 \cdot H_2O$			13	69
$MgSO_4 \cdot 7H_2O$			6.6	
$CaSO_4$			8.8	
$CaSO_4 \cdot 2H_2O$			38.0	
$FeSO_4 \cdot 7H_2O$	40		75	
$CoSO_4 \cdot 7H_2O$	40		27	
$NiSO_4 \cdot H_2O$	40		28	69
α-$NiSO_4 \cdot 6H_2O$	40		25	69
β-$NiSO_4 \cdot 6H_2O$	40		37	69
$NiSO_4 \cdot 7H_2O$	40		36	69
$ZnSO_4 \cdot H_2O$	40		28	69
$ZnSO_4 \cdot 6H_2O$			13	69
$ZnSO_4 \cdot 7H_2O$	40	Cyclotron	15	69
$Na_2S_2O_3 \cdot 5H_2O$		Ra–Be source	45	58
$Na_2SO_3 \cdot 7H_2O$			~55	6, 7
$Na_2SO_3 \cdot 7H_2O$		Cyclotron	55	69
$Na_2SO_3 \cdot 7H_2O$		Ra–Be source	52	58
Na_2SO_3		Thermal column	2.4	69
Na_2SO_3		Cyclotron	15	1
$Na_2S_2O_5$		Cyclotron	3	1
$K_2S_2O_5$		Cyclotron	10.7	1
$K_2SO_3 \cdot 2H_2O$		Cyclotron	26	1
$(NH_4)_2SO_3 \cdot H_2O$		Cyclotron	71	1
NH_4HSO_3	40	Cyclotron	30	1
$Na_2S \cdot 9H_2O$			65–95	6, 7
$Na_2S \cdot 9H_2O$		Cyclotron	30	69
K_2S		Cyclotron	6–11	69
CaS		Cyclotron	40–50	69
			[Orthophosphate (50)]	
KCNS		Ra–Be source	61	58
		Reactor	40	1
b. Aqueous solutions				
	Concn.			
Na_2SO_4	10%		54.2	69
$(NH_4)_2SO_4$	10%	Cyclotron	58.2	69
Na_2SO_3	10%	Cyclotron	89.2	69
$NaClO_4$	10%	Cyclotron	53.7	69
H_2SO_4	10%	Cyclotron	75.2	69
H_2SO_4	92.7%	Ra–Be source	45	58

[a] Nuclear reaction $S^{32}(n,p)P^{32}$. [b] In each experiment the separation method used precipitation as $MgNH_4PO_4 \cdot 6H_2O$.

6.6%. It therefore reached a yield similar to that obtained by irradiation at room temperature. A more detailed study of the rate of decrease of the non-orthophosphate fraction recovered at various annealing temperatures from solid $(NH_4)_2SO_4$ after irradiation in liquid air indicated that the process seemed to involve two stages: an initial very fast stage and a stage which at 5° is very slow.

The thermal annealing of neutron-irradiated crystalline sodium sulfite results in an oxidation reaction, which increases the fraction of P^{32} as orthophosphate. It was suggested that such oxidative annealing may proceed by interaction of P^{+3} ions with oxygen atoms formed in the recoil process or by radiolysis. However, since even neutron-irradiated sodium thiocyanate, which contains no lattice oxygen, undergoes oxidative annealing, it had to be concluded that lattice defects such a positive holes act as oxidants (1).

B. CHLORINE COMPOUNDS

The chemical forms of P^{32} formed by neutron irradiation of several crystalline chloride salts were investigated using the $Cl^{35}(n,\alpha)P^{32}$ reaction (6, 7).

Appreciable amounts of P^{32} were found in reduced forms in yields which differed for the sodium, potassium, or magnesium salts (see Table VII).

TABLE VII

CHEMICAL PRODUCTS OF RECOILING P^{32} IN SOLID INORGANIC CHLORIDE SALTS

Compound	Yield of labeled non-orthophosphate, %	Ref.
NaCl	60–70	6, 7, 69, 108, 109
KCl	*ca.* 50[a]	15, 16, 20, 69
NH_4Cl	29	69
$MgCl_2 \cdot 6H_2O$	7	69
$NaClO_2 \cdot H_2O$	1	69
$KClO_3$	1	69
$NaClO_4 \cdot H_2O$	0.8	69
$KClO_4$	1	69
NH_4ClO_4	0.5	69
$MgClO_4 \cdot 6H_2O$	3	69
KCl	12 (HPO_3^{-2})[b] 43 $(H_2PO_2^{-})$ 32 (PH_3)	81

[a] Depends on annealing conditions. [b] Orthophosphate, 13% yield.

In the neutron bombardment of potassium chloride (20) and of sodium chloride (108, 109) under low flux conditions, in the absence of air and moisture, the P^{32} formed by the $Cl^{35}(n,\alpha)P^{32}$ reaction was contained both in orthophosphate and in lower oxidation states, even in phosphine. The oxidation state was strongly affected by either X-ray or γ-irradiation.

γ-Irradiation of potassium chloride crystals prior to neutron irradiation caused a remarkable increase in the yield of P^{32} in lower valence forms (15, 16). The reducing action of ionizing radiation was explained to be due to electrons from F centers. This hypothesis was confirmed by comparing the rate of bleaching of the color of the crystals with the decrease in reduction of recoiling P^{32} atoms. The thermal annealing of neutron-irradiated potassium chloride at various temperatures caused at first an increase, followed by a decrease, in the yield of lower valence forms of P^{32} compounds. The oxidative reactions causing decrease in the non-orthophosphate fraction were shown to be due to positive holes formed as lattice defects, because potassium chloride, which had been irradiated with a D + T neutron source (which is almost free of γ-rays), did not undergo any appreciable annealing. On the other hand, after reactor irradiation (which involved also an intense γ-flux) potassium chloride was very sensitive to oxidative annealing (15, 16).

The chemical state of recoil products of the $Cl^{35}(n,\alpha)P^{32}$ reaction in liquid carbon tetrachloride was studied carefully, using a variety of irradiation and product separation procedures (58). About one-half of the radiophosphorus seems to be produced as orthophosphate and the rest in reduced and condensed forms of phosphorus oxyacids, because extraction of the irradiated carbon tetrachloride with a solution of sodium thiosulfate (1.0 *N*) yielded 45% in the form of orthophosphate. Other extractants (dilute NaOH or HNO_3) produced larger yields of orthophosphate—probably due to hydrolysis and oxidation of condensed and reduced forms of phosphorus initially present in the carbon tetrachloride. The fraction of radiophosphorus produced as orthophosphate was found to depend strongly on the presence of various substances during irradiation (see Table VIII).

TABLE VIII

EFFECTS OF ADDED SUBSTANCES ON THE VALENCE STATE OF P^{32} AFTER NEUTRON IRRADIATION OF CCl_4 (58)

Added substance (ml.) to 1000 ml. of CCl_4	P^{32} as orthophosphate, %
None	98
H_2O (0.8)	68
NH_4OH, 25% (0.8)	27
Acetone (10)	86
NH_3 (satd.)	14
H_2O (satd. with Br_2) (10)	98

The considerable lowering in the orthophosphate yield by the presence of water or ammonia has already been observed in the irradiation of sulfate and is best explained by hydrogen-abstraction reactions of the recoiling P^{32} atom, causing formation of P–H compounds. The annealing effect of prolonged neutron irradiation of carbon tetrachloride caused an appreciable increase in the yield of radiophosphorus as orthophosphate (see Table IX).

TABLE IX
DEPENDENCE OF THE YIELD OF P^{32} AS ORTHOPHOSPHATE ON THE TIME OF IRRADIATION

Irradiation time, hr.	Yield, %	
	Dry CCl_4	0.22 ml. H_2O/1000 ml. CCl_4
12	84	47
24	89	50
48	92	59
144	98	56

Neutron bombardment of S_2Cl_2 and analysis of the products by distillation or chromatography showed that the radiophosphorus is formed mainly as thiophosphoryl chloride, $PSCl_3$. The radiophosphorus in this case is due to both the S^{32}(n,p) reaction and the Cl^{35}-(n,α) reaction (58).

The chemical state of radiophosphorus formed after the irradiation of crystalline potassium chloride with high energy protons (660 Mev.) has been examined (81–83). The activity observed was initially mainly hypophosphite (about 70%) and a smaller yield of orthophosphate and phosphite (see Table VII). The kinetics of oxidation of the hypophosphite and phosphite to orthophosphate due to annealing at various temperatures from 200 to 400° were studied.

VII. CONCLUSION

The results of radiative thermal neutron capture in gaseous and liquid phosphorus compounds indicate that primary retention does not occur to any appreciable extent. Understanding of the chemical effects of neutron capture in solid phosphates will require more information of the physics and chemistry of radiation damage in these compounds.

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