

AN INVESTIGATION OF NEUTRON-IRRADIATED
THIOPHOSPHORYL CHLORIDE

by

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A. B., Kansas State Teachers College
Pittsburg, Kansas, 1951

A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

1955



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INTRODUCTION

Chemical effects accompanying nuclear reactions are interesting, but not yet well understood. Product atoms exhibit abnormally high kinetic energy or electrical charge or both. In addition, orbital electron excitation may occur. Any of these phenomena may produce chemical effects. The kinetic energy is acquired in the recoil process following particle or photon emission, momentum being conserved. The electrical charge results from charged particle emission, electron capture, internal conversion or Auger electron emission.

Since chemical bond energies are seldom more than a few electron volts in magnitude, the high recoil energies in many nuclear reactions allow rupture of not only the bond or bonds holding the product atom in its parent molecule, but also many bonds in neighboring molecules before thermal energies are reached.

The number of product atoms formed in nuclear reactions is so small that regardless of the nature of the end-product molecules, they cannot be detected by ordinary chemical means. However, separation by use of carrier methods using macro amounts of possible products can be accomplished provided two important criteria are met: 1.) the product atoms must be radioactive, and 2.) the various possible chemical forms of the

product atom must not thermally exchange. The first of these is to allow identification by radioassay methods while the second is to assure proper chemical separation by means of the carriers as well as to give molecular species indicating the true chemical effects of the nuclear reactions.

Hein and McFarland in 1952 (17) used neutron-irradiated PCl_3 in the synthesis of the insecticide parathion, O-O-di-ethyl O-p-nitrophenylthiophosphate. The product showed not only β^- activity from P^{32} , as desired, but also a β^- activity found to be that of S^{35} . Consideration of the chemical steps involved in the synthesis required the S^{35} to be present in the irradiated PCl_3 , either as elemental S^{35} atoms, molecules of $\text{PS}^{35}\text{Cl}_3$ or in a form which could thermally exchange to provide them.

Subsequent investigation by Conn (9) on neutron-irradiated samples of PCl_3 showed evidence for formation of $\text{PS}^{35}\text{Cl}_3$ molecules (where the P could be stable P^{31} or radioactive P^{32}) as well as elemental S^{35} and labeled sulfur monochloride. A preferential reaction yielding $\text{P}^{32}\text{S}^{35}\text{Cl}_3$ was hypothesized. Results of that work indicated the desirability of studying other phosphorous-sulfur-chlorine compounds, the present thesis being second in a contemplated series.

PSCl_3 was chosen as the compound to be studied because it was felt that not only would it be of interest in its own right

but that the results might also be compared with those obtained for PCl_3 and S_2Cl_2 and might aid in continuing their investigations.

The major objectives of the study were to gain qualitative knowledge of nuclides and molecular species produced in the irradiation and quantitative knowledge, where possible, concerning nuclide distribution among the various molecular products. A search for the presence of doubly-labeled $\text{P}^{32}\text{S}^{35}\text{Cl}_3$ was proposed, although techniques had not yet been developed for such a search.

In addition, a short study of possible exchange of sulfur atoms between elemental radioactive S^{35} and inactive PSCl_3 was undertaken. This might be of help in evaluating molecular product identifications when viewed in conjunction with other exchange reactions being investigated at the time.

Maddock in 1953 (30) in a survey article concerning the chemical effects of nuclear transformations said that

although qualitatively satisfactory interpretations of most of the effects have been advanced, the most satisfactory identification of the mechanisms involved cannot be expected until more critical experiments have provided more accurate quantitative data.

This statement and similar ones in the literature gave impetus to the study of neutron-irradiated thiophosphoryl chloride.

LITERATURE SURVEY

General

In 1934 Szilard and Chalmers (38) described a chemical technique for separation of radioactive isotopes produced by neutron irradiation of the inactive element. The element was initially combined in such manner that the product atom, after recoil, had little chance of being recaptured to form the original compound. In the classic example, ethyl iodide was irradiated, yielding free radioactive iodine which was removed as silver iodide.

Since 1934 more than a hundred studies have been made of Szilard-Chalmers type reactions, most of them using radioactive neutron capture. Willard (40) in his 1953 review article attributed this to a number of factors, among which were 1.) the relative availability of neutrons, 2.) the relative ease of using them under conditions where radiation damage and temperature effects were not serious, 3.) the fact that the (n, γ) process was capable of producing a number of radioactive species with chemical properties which were suitable for studies of this type and 4.) the favorable cross-sections for the (n, γ) process. In general, Szilard-Chalmers reactions are used to produce a radioactive isotope with high specific activity. It should be noted in passing that the success of a true Szilard-Chalmers type reaction is dependent on a number

of factors:

1. In the process of formation, the radioactive atoms must be broken loose from the parent ions of molecules.
2. The element to be activated should be capable of existence in at least two mutually stable forms which are chemically separable.
3. The forms should not undergo rapid isotopic exchange.
4. The most suitable target form will probably be a fairly complex molecule or ion or at least one that can not be resynthesized under irradiation conditions.

At the same time it should be noted that a perfect Szilard-Chalmers reaction is not always desired. As a matter of fact, for production of appreciable quantities of labeled mother molecules the reverse effect is needed.

A study of incomplete reactions has provided the richest field for study and conjecture. Much of the literature deals with studies of such incomplete reactions and attempts to evolve reaction mechanisms which successfully account for the results obtained.

Comprehensive reviews of this matter have been given by Barnes, et al. (2), Williams (41), Maddock (29), McKay (32), Broda (6), Green (16) and Willard (40). In addition, the references listed by Conn (9) in his Master's thesis concerning PCl_3 are equally applicable to PSCl_3 .

References dealing with the chemical aspects of Szilard-Chalmers reactions such as product species, mother-molecule

reformation and effects of environment such as pH, chemical purity, molar concentrations and the like are of some help, but the results are rather specific for a single compound or homologous series of compounds. Data concerning physical conditions such as conditions of state, presence of electrostatic fields, temperature and pressure are helpful, but again are apt to be of a specific nature.

Because a complex molecule is reformed with greater difficulty, leading to a more successful Szilard-Chalmers reaction, much of the literature deals exclusively with organic target materials. These references are of little direct value for the PSCl_3 system, but help establish general principles.

A number of papers are listed in the sections that follow to acquaint the reader with results to date and the attempts to generalize from them.

Mechanisms

Until recent years the chemical effects of thermal neutron capture, the Szilard-Chalmers effect, were ascribed exclusively to mechanical recoil, even though no direct observation of such recoil had been made. Magnusson (31) irradiated gold in a very thin foil and was able to obtain recoil-separated product atoms on a small scale from the (n, γ) reaction involved. Yosim and Davies (42) have since done work which indicated that most of the gold atoms escaping from the foil were positively

charged. If internal conversion occurred in the foil surface, the charge would be neutralized before the atom escaped so they reasoned that the internal conversion process must have occurred sufficiently later to have allowed escape.

The impact of thermal neutrons, having an average kinetic energy of only 0.025 ev, could not be the cause of bond rupture since most chemical bonds are about 2-5 ev or so in magnitude. (Pauling, 35). The kinetic energy obtained when a ray is emitted, following neutron capture is given by

$$E_M = \frac{536 E_\gamma^2}{M} \text{ ev}$$

where E_γ is expressed in mev and M is the product atom mass in atomic mass units. The result may be the acquisition of enough kinetic energy to rupture one or more bonds. Development of this fundamental formula can be found in nearly any recent text in radiochemistry. Multiple γ ray emission might conceivably result in partial cancellation of the recoil energy but in 1953 Willard (40), from evidence obtained in gas phase studies, said that γ ray cancellation is relatively unimportant in protecting parent molecules from rupture.

A typical example of recoil energy imparted to the product nuclide by γ emission and the energies involved is reported by Kikuchi, et al. (21). The γ ray emitted in the $\text{Cl}^{37}(\text{n}, \gamma)\text{Cl}^{38}$ process has an energy of 6.2 mev and the value of E_M calculated as above was 543 ev, enough to rupture many bonds.

Proton or other heavy particle emission leads to still higher values of recoil energy. Complicated but exact relationships were derived by Libby (26) for use in calculating these energies.

The study of what happens to the recoiling product atom as evidenced by its final chemical state has led to formation of at least two hypotheses to explain mechanisms involved in Szilard-Chalmers reactions. These are the so-called "billiard ball collision-epithermal collision" hypothesis and the "nest of radicals" hypothesis.

In the billiard-ball collision theory, recoiling atoms lose their energy in elastic collisions with single atoms, according to Libby (27). This assumes that the transfer occurs as if the atoms were isolated, as in the gas phase. The fractional energy loss can be calculated by

$$\frac{E_{\text{loss}}}{E_{\text{initial}}} = \frac{4MM_1}{(M+M_1)^2} \cos^2 \theta$$

where M and M_1 are the masses of the impinging and the struck atom, respectively, and θ is the angle between their paths after collision. A head-on collision between atoms of any nearly equal masses would project the struck atom into the medium, leaving the de-energized impinging atom in a solvent "cage" with the radical just formed. Combination of the two would have a high probability.

Friedman and Libby (14) found that dibromopropanes were

formed from neutron irradiation of propyl bromide. To account for this and similar effects it was postulated that when and if the energy of the product atom were reduced to about 10 ev, as by collisions with lighter atoms, the halogen atom could transfer energy to molecules as a whole in inelastic collisions. Bond rupture from vibrational excitation might follow and the halogen atom left in the solvent cage could react with the radical to form a stable molecule. If a C-H bond had been broken, the halide taking its place would give rise to a species different from the mother molecule. These are the "epithermal collision" reactions.

Willard (40) cited a number of reasons, relating to specific cases, where the billiard ball collision-epithermal collision hypothesis failed to account for reliable results. He then discussed the "nest of radicals" hypothesis where the newly formed recoil atom, possessing several hundred ev of recoil energy loses its energy in a series of collisions in a limited space. This he ascribed to the fact that the struck molecules were backed by a close-packed often intertwined wall of other molecules. The result was the indiscriminate breaking of many bonds in the original vicinity of the energetic atom.

When the recoiling atom had reduced its energy below that needed to break bonds it would find itself in or adjacent to a cluster of radicals in high concentration. It could

combine with a radical or with impurities such as oxidizing or reducing compounds or alternatively might enter stable combination by a thermal process after diffusion in thermal equilibrium with the medium.

Impurities can play an important and often misleading role in either interpretation. In 1949, Friedman and Libby (14) reported the organic yield of n-propyl bromide as 50 per cent, using samples which were redistilled and which had refractive indices that checked within one part in ten thousand. In 1952, Fox and Libby (13) in the same laboratories reported a yield of 35 per cent if the material were more carefully purified before irradiation. The concentrations of impurity which can affect a reaction are so low that no ordinary analytical technique will suffice to determine them. Only when similar results are obtained using starting materials purified in widely different manners can any degree of confidence be had as to purity of materials.

Chemical Results

As yet, not many chemical studies of Szilard-Chalmers reactions have given results from which broad generalizations can be drawn. Results for one system are of little help in predicting the outcome of other systems.

A few reports, however, served to affirm or negate theories proposed to explain mechanisms, retentions and results

in general. Gas phase reactions were studied because of the isolated molecules involved. Primary effects were more easily observed or measured. Suess (37) using ethyl bromide-hydrogen bromide mixtures was able to show that bond rupture resulted from nearly every neutron capture as predicted by energy considerations. Greater than 97 per cent of the bromine atoms were found as inorganic bromine. He also found that addition of acetylene increased the fraction of radiobromine found organically combined. The increase was in proportion to the partial pressure of acetylene but appeared independent of the partial pressure of hydrogen bromide. Application of a strong electric field (1000 volt potential) had no marked effect on the distribution of activity.

Bohlman and Willard (4) found no evidence of retention when carbon tetrachloride or tetrachloroethylene were irradiated in the gas phase.

Another result of general importance was reported when Wexler and Davies (39) demonstrated in 1948 that the (n, γ) process can lead to charged product atoms. Ethyl bromide was used at low pressures and radioactive bromine atoms appeared on a cathode when 4000 volts were applied.

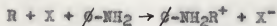
Studies of retention are important. In most of the organic halide work reported, retention was about 50 per cent in liquid systems. From a consideration of energies involved

nearly all of the radioactive halide should have been inorganically combined. This was observed for gas phase reactions, as we have just discussed.

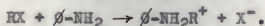
Lu and Sugden in 1939 (28) experimented with the effects of free halogen addition on retention as organic halides. From one to three per cent free halogen was added before irradiation. This led to an increase in the amount extractable if the organic halide were aliphatic but seemed to have little effect if the halide were aromatic.

The same workers showed that varying the extracting agent had a large effect in the end results. For example, water extraction of irradiated ethylene bromide gave 45 per cent of the radioactive Br^{80} as inorganic halide whereas 15 per cent sodium hydroxide extracted 51 per cent and copper foil extracted only 18 per cent.

On the assumption that phenol or aniline would react preferentially with recoil halogen atoms, they added small amounts of each to various solutions. Phenol seemed to have no effect but aniline had a marked effect, tripling the amount extracted by 5 per cent hydrochloric acid from irradiated bromobenzene. They postulated a reaction between a free organic radical, the free halogen recoil atom and a molecule of aniline which gave a substituted ammonium ion and a halide ion



Alternatively, if the recoil atom recombined with the organic radical to yield a halide molecule, this molecule could retain enough vibrational energy to undergo a reaction



Dilution has also been shown to have a marked effect on retention. Libby (27) and Glückauf and Fay (15) found that sufficient dilution of organic solutions reduced retention of the radioactive halogens to zero. Libby showed, for instance, that as the mole per cent of carbon tetrabromide was decreased from 100 to 0.064 per cent by dilution with ethanol that the per cent of radiobromine organically combined decreased from 60±5 per cent to 0±2 per cent.

As can be seen, most of the literature pertains to (n,γ) reactions. The recoil energies from particle emission are, in general, much higher but Willard (40) mentions that there is no good reason why the ultimate chemical products should be different in an (n,p) reaction than if an atom of the same final atomic number were activated by an (n,γ) process.

A few references in the literature were of more direct help in considering the PSCl_3 system. Caillat and Sue (7,8) in 1950 found that the P^{32} produced in the $\text{Cl}^{35}(\text{n},\alpha)\text{P}^{32}$ reaction with alkali chlorides was divided about evenly between P(V) and lower valences and that the ratio of P(V) to lower valences was increased by presence of water in the crystals. Heating to 350° C after irradiation lowered the ratio. Fiskill, et al. (12) in 1952 examined the chemical species produced by

irradiating calcium phosphates and found most of the P^{32} had recombined in the mother molecules, most of the remainder appearing in the hypophosphate. Aten, et al. (1) in 1952 published the results of a study of the distribution of P^{32} activity between orthophosphate, pyrophosphate, phosphite and hypophosphite following neutron irradiation of the monohydrates of sodium pyrophosphate ($Na_4P_2O_7 \cdot H_2O$) and disodium hydrogen phosphate ($Na_2HPO_4 \cdot H_2O$).

A number of workers have shown that KCl exposed to neutrons without exclusion of air, when dissolved in water containing $SO_3^{=}$ and $SO_4^{=}$ carriers, yields the S^{35} in the $SO_4^{=}$ fraction. Koski (24) reported in 1949 that if stringent methods were used to degas the crystals before irradiation, 35 per cent of the S^{35} could be recovered in sulfide carrier. Croatto and Maddock (11), however, could not reproduce these results. Willard (40) in his 1953 review article states that a doctoral thesis presented by R. Milham in 1952 at the University of Wisconsin discussed similar work, using vacuum sublimed crystals of KCl and thoroughly degassed carrier solutions. Ninety per cent of the sulfur could be extracted as sulfide if the crystals were dissolved in aqueous sulfide, but only 30 per cent as sulfide if the carrier was added after dissolving the crystals in water. The remainder appeared as sulfate.

Exchange Reactions

If exchange occurs during the time between atom recoil and sample assay, the results are apt to be confusing or meaningless. The literature is of little help at this time in predicting exchange. A few references dealing with phosphorous, sulfur and chlorine can be found, but most of them apply to systems quite different than PSCl_3 .

Cookey and Yost (10) in 1940 reported exchange between S_8^{35} and S_2Cl_2 with a half-time for the exchange of about 30 minutes. They postulated a slow, reversible dissociation of S_8^* into S_6 and S_2^* , followed by rapid exchange between the S_2^* and the S_2Cl_2 .

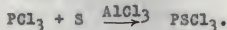
Using Cl^{38} , Koskoski and Fowler (25) found exchange between Cl_2^* and PCl_3 with less than 70 seconds half-time for exchange, and exchange between Cl_2^* and PCl_5 with less than 40 seconds half-time. They also concluded that all five halogens on a PX_5 molecule were equally reactive, with respect to exchange.

MATERIALS AND METHODS

Source of the PSCl_3

The PSCl_3 used in these studies was synthesized from commercial PCl_3 and elemental sulfur according to the method

reported by Knotz (23). The PCl_3 was redistilled for purification and removal of possible products of hydrolysis. The synthesis, at the boiling point of PCl_3 , was accomplished by refluxing in the presence of anhydrous aluminum chloride according to the equation



Use of a slight excess of sulfur assured the absence of any large amount of unreacted PCl_3 . The reaction was sensitive to the relative amount of AlCl_3 , too little preventing reaction at all and too much resulting in a violent reaction and loss of product from the top of the reflux condenser. Caution was in order.

The PSCl_3 was distilled twice for purification and a 25 ml. portion shipped to Oak Ridge National Laboratories for irradiation. For irradiation purposes, approximately 5 ml. aliquots of PSCl_3 were sealed off in quartz ampoules which in turn were put into aluminum cans for irradiation in the X-10 reactor for one week periods. It was interesting to note that the ampoules emerged from the reactor with the purple color of amethyst. Colorless conditions could be restored by the application of heat, as from a Bunsen flame.

Precise information as to irradiation conditions was not available but information received in private correspondence from the Oak Ridge laboratories indicated the overall neutron flux in the 50 per cent zone of the reactor was about 4.3×10^{10}

neutrons/cm²/sec for neutron energies above 0.6 mev and the flux above 2.6 mev as measured for the same zone was 1.2×10^{10} neutrons/cm²/sec.

Separation Methods

Fractional distillation at atmospheric pressure was the method used in separating chemical species. This method had been used by Conn (9) in work on the PCl₃ system. Other methods proved less successful because of hydrolysis or, in the case of filter-paper chromatography, reaction with cellulose. Metroware equipment with ground-glass joints throughout was used for the distillations. A silicone lubricant, Dow-Corning stopcock grease, was used on all ground-glass surfaces to prevent possible entrance of moisture-laden air and the chance for hydrolysis to occur. The only connection with the surrounding air was through a drierite filled U tube connected to the adaptor.

The distillation head was packed with Raschig rings for more efficient separations. Most fractions of distillate were small, 5 ml. or less, and special receiving flasks were constructed, utilizing the bottom halves of 10 ml. calibrated centrifuge tubes, to the tops of which were sealed 19/38 standard taper ground-glass outer joints which allowed direct connection to the distillation equipment. A cottonseed-oil bath was used to provide uniform heating of the distillation flask.

Quantities of inactive materials were used as carriers if the active forms of the same materials could be present in samples to be distilled. In this manner, troubles encountered in anomolous behaviour of micro or trace amounts of the materials were minimized. Some degree of assurance that even traces of radioactive species would appear in distillates at the proper temperatures was obtained.

Identification Methods

Standard methods of radioactive assay were employed throughout. A Berkeley decimal scaler, model 2000, was used in conjunction with a lead-shielded counting chamber housing a thin-end-window Geiger-Mueller tube of 1.9 mg/cm^2 areal density. The tube was operated at 1250 volts. A set of fixed-position shelves in the lead chamber allowed the use of a fixed "geometry" or radiation yield by counting only those rays and particles contained in a definite solid angle with respect to the sample.

A radium D and E standard, calibrated by the National Bureau of Standards, was used to determine the geometry for the counting conditions by counting the sample on a given shelf, calculating the disintegration rate of the standard on the counting day and using the formula

$$\% \text{ geometry} = \frac{\text{count rate} \left(\frac{c}{\text{time}} \right)}{\text{disintegration rate} \left(\frac{d}{\text{time}} \right)} \times 100$$

The standard was counted at least once during any period of

sample assay to check for abnormal fluctuations due to tube ageing, faulty scaling circuits, counting-chamber contamination and the like.

Counting errors were held constant throughout wherever possible to simplify calculations and comparisons. The use of round copper sample-mounting planchets 2.5 cm. in diameter and 0.0431 cm. thick for all counting samples reduced variations due to back-scattering. Self-absorption differences were cut down by use of uniform sample sizes and attempts were made to apply all samples to planchets in a set manner. The samples were of a size large enough to allow convenient counting times but small enough to avoid excessive coincidence losses. No dead-time corrections were made because of the relatively low counting rates involved.

Counting Sample Preparation

Counting aliquots were measured and transferred by means of calibrated micro-pipettes. Preparation of counting samples involved removal of the accurately measured aliquots, oxidation of phosphorus and sulfur in the various compounds to phosphates and sulfates while simultaneously converting the materials to non-volatile sodium salts with nitric acid and sodium nitrate. The converted materials were diluted to specified volumes and duplicate or triplicate aliquots were removed for counting. Where specific activity of a material to be

assayed allowed 25λ was removed ($1\lambda = 10^{-6}$ liters), converted directly in a 10 ml. volumetric flask and diluted to the 10 ml. mark after which 25λ counting aliquots were withdrawn and applied to the copper planchets. The samples were applied as a series of small droplets to the planchet surfaces to increase surface area and to decrease sample thicknesses, thereby reducing self-absorption losses. The counting samples were dried slowly on the planchets under an infra-red heat lamp and stored in a dust-free drawer until they were counted.

With solutions containing more than one activity of similar nature but different energies, it was possible to assay for one or both of the activities with a single counting sample by using calibrated aluminum absorbers available in the laboratory. When an absorber of sufficient thickness to absorb all the weaker radiation was interposed between the sample and counting tube, the activity measured was that of the stronger activity, modified by a factor to account for the actual absorption of a portion of the stronger activity by the aluminum. The amount of the weaker activity present could be determined by subtracting the corrected value of the stronger activity from the total value, obtained by removing the aluminum absorber. This technique was useful for assay of samples containing the weak β emitter S^{35} ($E_{\max.} = 0.167$ mev) in the presence of the stronger β emitter P^{32} ($E_{\max.} = 1.701$ mev).

EXPERIMENTAL WORK AND RESULTS

Nuclear Reactions

Before any actual laboratory work was done predictions were made as to the most probable outcomes of the irradiation of PSCl_3 , based on results of the study of PCl_3 and what other information could be gleaned from the literature.

The stable isotopes which compose PSCl_3 , and their relative isotopic abundances, according to the latest revision of the Table of Isotopes published by Hollander, et al. (18) are given in Table 1.

Table 1. Isotopic abundances.

Isotope	P^{31}	S^{32}	S^{33}	S^{34}	S^{36}	Cl^{35}	Cl^{37}
Abundance	100%	95.018%	0.75%	4.215%	0.017%	75.4%	24.6%

With these nuclides and abundances in mind, one could postulate many nuclear reactions producing radioactive nuclides as the result of neutron irradiation, among which might be:

- | | |
|--|--|
| (1) $\text{P}^{31} (n, \gamma) \text{P}^{32}$ | (8) $\text{Cl}^{35} (n, \gamma) \text{Cl}^{36}$ |
| (2) $\text{P}^{31} (n, p) \text{Si}^{31}$ | (9) $\text{Cl}^{35} (n, p) \text{S}^{35}$ |
| (3) $\text{P}^{31} (n, \alpha) \text{Al}^{28}$ | (10) $\text{Cl}^{35} (n, \alpha) \text{P}^{32}$ |
| (4) $\text{S}^{32} (n, p) \text{P}^{32}$ | (11) $\text{Cl}^{37} (n, \gamma) \text{Cl}^{38}$ |
| (5) $\text{S}^{33} (n, p) \text{P}^{33}$ | (12) $\text{Cl}^{37} (n, p) \text{S}^{37}$ |
| (6) $\text{S}^{34} (n, \gamma) \text{S}^{35}$ | (13) $\text{Cl}^{37} (n, \alpha) \text{P}^{34}$ |
| (7) $\text{S}^{36} (n, \gamma) \text{S}^{37}$ | |

This list, as well as others which might be proposed, was greatly reduced by consideration of such factors as isotopic abundances, neutron energies, neutron capture cross-sections and radioactive half-lives. A consideration of half-lives, for instance, showed that reactions (3), (7), (11), (12) and (13) were of no importance in these studies since the half-lives of Al^{28} , S^{37} , Cl^{38} and P^{34} were listed in the Table of Isotopes (18) as 2.27 minutes, 5.04 minutes, 37.29 minutes and 12.4 seconds, respectively. There was no possibility of detecting these nuclides at the time of first assay, three days after removal from the reactor. In ten half-lives only $1/1024$ (or about 0.01%) of an activity remains. A three day period was long compared to ten half-lives of these nuclides.

Reaction (8) would give Cl^{36} , a nuclide with a half-life listed as 4.4×10^5 years. As only a few Cl^{36} atoms would be formed during a one week irradiation, it was not possible to detect this activity.

Reactions (2) and (5) would lead to the formation of 2.62 hour Si^{31} and 25.4 day P^{33} , respectively. Si^{31} is a β^- -emitter whose energy is 1.471 mev but because of its half-life it would be virtually gone when a sample arrived for assay. P^{33} with its relatively weak 0.270 mev β^- -emission would be formed from S^{33} , whose isotopic abundance was only 0.75 per cent. It was not surprising that neither Si^{31} nor P^{33} was found experimentally.

Eliminating from discussion the reactions just shown to be of little practical importance, the remaining reactions would produce only two nuclides. Reactions (1), (4) and (10) would produce P^{32} , a 1.701 mev β^- emitter whose half-life was listed as 14.3 days and reactions (6) and (9) would produce S^{35} , a 0.167 mev β^- emitter having a half-life of 87.1 days. Neutron cross sections should be considered when discussing nuclide production by these methods. Cross sections with thermal neutrons for the two reactions which proved to be most important in the production of P^{32} and S^{35} are given by Seren, et al. (36) as 0.169×10^{-24} cm² for the $Cl^{35}(n,p)S^{35}$ and 0.23×10^{-24} cm² for the $P^{31}(n,\gamma)P^{32}$ reaction. Other pertinent cross section values are listed in the appendix. The half-lives and energies of P^{32} and S^{35} allowed convenient assay.

Nuclides Found Present

The results of an energy study of a typical sample as received from Oak Ridge, and before separations, are shown in Plate I. Calibrated aluminum absorbers were used in the study and a comparison with curves obtained using radioactively pure materials indicated the presence of P^{32} and S^{35} .

The results of a half-life study on the same material is shown in Plate II and this information confirmed the presence of P^{32} and S^{35} . No indications of the presence of other nuclides were obtained.

In Plate II the values of P^{32} activity, obtained by filtering out S^{35} activity from a composite sample with a 34.5 mg/cm² aluminum absorber, were multiplied by a factor of 1.20. This was to correct for the absorption of a portion of the P^{32} activity by the absorber. The factor 1.20 represents the average value obtained in a number of determinations, using different samples of radioactively pure P^{32} . All samples were counted under the same conditions (geometry, sample size, sample backing and the like). Extreme values obtained were 1.19 and 1.26, with the average at 1.20.

A typical set of counting data, obtained on March 9, 1954, is given in Table 2.

Table 2. Effect of aluminum absorber on P^{32} activity.

Absorber (mg/cm ² Al)	Time	Counts	C/min.	C/min. : less bkgd.
0	5 min.	19,200	3840	3824
34.5	5 min.	16,010	3202	3186

From the values in Table 2 the ratio of P^{32} activity without the absorber to that measured with the absorber was 3824/3186, or 1.20. All P^{32} values measured through the 34.5 mg/cm² aluminum absorber were multiplied by the factor, 1.20, to correct for absorption losses.

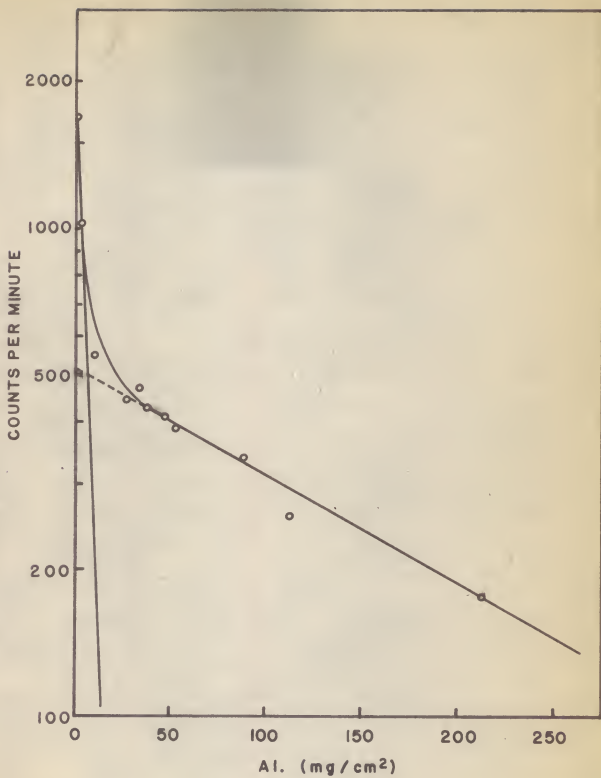
All radioactive assay was done from a fixed position,

EXPLANATION OF PLATE I

β^- Energy Study by Absorption Technique, Neutron-Irradiated PSCl_3

The sharp break in the curve indicates the presence of two distinct activities. The component yielding the more horizontal portion was shown, by comparison with curves obtained using pure materials, to be the nuclide P^{32} . Subtraction of the P^{32} curve from the composite curve gave the resultant nearly vertical line, due to S^{35} activity. E_{max} for P^{32} is 1.701 mev; E_{max} for S^{35} is 0.167 mev.

PLATE I

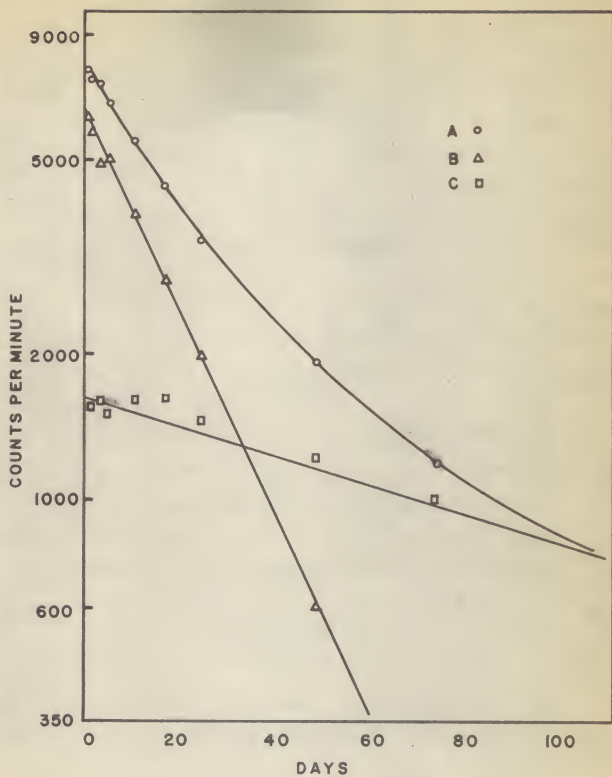


EXPLANATION OF PLATE II

Half-life Study, Neutron-Irradiated PSCl_3

Curve A was obtained without the use of absorbers, and its curvature indicates activity due to more than one component. Curve B was obtained by the use of a 34.5 mg/cm^2 Al absorber. The experimental values were multiplied by 1.20 to account for absorption of part of the strong β^- activity. The half-life of 14.3 days indicates presence of P^{32} . Curve C is that obtained by subtracting P^{32} activity from total activity. The resultant 87.1 day half-life indicates S^{35} .

PLATE 11



relative to the end of the counting tube. Since particles and rays were emitted in every direction from each counting sample, only a small, fixed portion of them was included in the solid-angle intercepted by the tube end. To determine this small, fixed portion known as radiation yield or "geometry", a sample of Ra D and E (the radionuclides Pb^{210} and Bi^{210}) was used. This sample had been calibrated by the National Bureau of Standards and on May 1, 1950, was certified to have a disintegration rate of 100.4 d/sec. The calculated disintegration rate for March 5, 1954 was 88.1 d/sec, or 5286 d/min. When counted in our fixed position it gave an average of 323 counts/min. Comparing the count rate to the disintegration rate, a geometry of $323/5286$ or 6.1 per cent was obtained. Since this factor was constant throughout, any comparisons of counts/time would give the same results as comparisons of disintegrations/time.

Structure of PSCl_3 Molecule

A consideration of the physical construction of the PSCl_3 molecule was necessary for predicting and interpreting results of neutron irradiation. The structure of PSCl_3 was found similar to that of POCl_3 , a tetrahedron with the phosphorous atom contained within. Kekulé (20) and others imagined the POCl_3 molecule to be $\text{Cl}_2\text{P}-\text{OCl}$ but this was disproved when Brockway and Beach (5) found POCl_3 to be tetrahedral with the phosphorus-halide bonds all equal in length. The same held true

for PSCl_3 . Beach and Stevenson (3) have found that in PSCl_3 the P-Cl distance is $2.02 \pm 0.02 \text{ \AA}$. The P-S distance, they found, was $1.94 \pm 0.03 \text{ \AA}$ which was close to the double-bond value of 1.95 \AA , showing that the bond had a large amount of double-bond character. Brockway and Beach (5) also found that in molecules similar to POCl_3 the angles in the halogen-phosphorus-halogen structures are close to 106° instead of $109^\circ 28'$, the ordinary tetrahedral angles. This they also attributed to the double-bond character of the P-O (or P-S) bond.

It should be noted that if the S atom were removed from PSCl_3 , only slight rearrangement would be necessary to attain the PCl_3 configuration, with its P-Cl bond distances of $2.00 \pm 0.02 \text{ \AA}$ and Cl-P-Cl angles of 101° . These are the values listed by Pauling (35) for the stable configuration of PCl_3 .

The atoms of the PSCl_3 molecule are of nearly equal mass. This means that the decrease in energy per elastic collision would be fairly uniform and formation of labeled molecules would result from the billiard-ball type collisions. Although many compounds might feasibly be formed, only those species thermally stable at ordinary conditions of temperature and pressure would be expected to remain at the time of separations and assay, three or more days after irradiation.

Possible Product Species

Based on the work of Conn (9) on PCl_3 and on pure conjecture, a list of possible products was drawn up which included unreacted or stable material such as PSCl_3 , PCl_3 , PCl_5 , SCl_2 and S_2Cl_2 as well as radioactive species such as $\text{P}^{32}\text{SCl}_3$, $\text{PS}^{35}\text{Cl}_3$, $\text{P}^{32}\text{S}^{35}\text{Cl}_3$, P^{32}Cl_3 , P^{32}Cl_5 , S^{35}Cl_2 , $\text{S}^{35}_2\text{Cl}_2$, $\text{S}^{35}\text{SCl}_2$ and S^{35} . The varieties of radioactive PSCl_3 were of interest because mother molecule reformation was certain to take place, but the relative extent was not known and had to be experimentally determined. A unique problem in connection with the active forms of PSCl_3 was the separation and identification of various types of the same molecule. Chemical separation was impossible, of course, and radioactive assay methods would not indicate whether a decaying P^{32} atom was associated with a radioactive S^{35} atom or an atom of one of the stable sulfur isotopes.

Since molecular breakup, or at least loss of identity as PSCl_3 , accompanied the radioactive decay of any of the active atoms, it could be seen that $\text{P}^{32}\text{SCl}_3$ molecules would disappear with the 14.3 day half-life associated with P^{32} while $\text{PS}^{35}\text{Cl}_3$ would disappear with the 87.1 day half-life of S^{35} . $\text{P}^{32}\text{S}^{35}\text{Cl}_3$ molecules, however, had an opportunity of disappearing because of P^{32} decay or also because of S^{35} decay. In addition, there was a chance that both its radioactive components might decay

simultaneously. The anomolous result, produced by the three possible methods of break-up of the doubly-labeled molecules, would be the loss of $P^{32}S^{35}Cl_3$ at a rate even faster than the 14.3 day half-life of P^{32} labeled molecules.

This called to mind the cases of branched chain decay of certain nuclides in the natural radioactive series. There nuclides can decay by either of two independent methods. For example, consider the case of thorium C (Bi^{212}) in the $4N$ series, 66.3 per cent of which produces thorium C' (Po^{212}) by β -decay while the remaining 33.7 per cent forms thorium C'' (Tl^{208}) simultaneously by α decay. The single half-life value of 60.5 minutes listed in the Table of Isotopes (18) represents the rate of disappearance of the thorium C but not the rate of formation of either specific product. It has been found that for a general case



where a radionuclide species A decays with a characteristic decay constant $\lambda_b (= .693/t_{1/2})$ to produce a species B and at the same time decays with a decay constant λ_c to produce another species C, the effective half-life of A is given by

$$t_{1/2} = 0.693/(\lambda_b + \lambda_c).$$

If the same type reasoning was applied by analogy in the case of doubly-labeled $PSCl_3$, where half-lives of 14.3 days and 87.1 days were involved, use of the general formula just

given led to a calculated effective half-life of 12.4 days. In other words, evidence for disappearance of PSCl_3 at a 12.4 day half-life rate would indicate presence of the doubly-labeled species. Whether or not the analogy was valid the fact remains that doubly-labeled PSCl_3 , having more than one method of breaking up, would disappear at a rate faster than that due to decay of either P^{32} or S^{35} . This assumes that thermal exchange did not take place between labeled fragments and inactive PSCl_3 , resulting in the production of more labeled PSCl_3 . Exchange is discussed later.

R. E. Hein derived the following relationship for the case from fundamental principles:

$$N_t = N_1 e^{-\lambda_1 t} - [N_1(1 - e^{-\lambda_2 t})] + f$$

where N_t was the number of labeled molecules which remained intact at time t , N_1 was the number of labeled molecules originally present, λ_1 was the characteristic decay constant ($=0.693/t_{1/2}$) and f was a factor to correct for the possibility of breakup by both possible methods simultaneously. He later determined the value of f to be $N_1[e^{-\lambda_1 t}(1 - e^{-\lambda_2 t})]$. Use of the relationship, by substitution of values of N_t , gave an effective half-life of 12.6 days for doubly-labeled PSCl_3 .

Regardless of the method used, the loss of doubly-labeled PSCl_3 at a rate faster than that due to P^{32} decay was obtained.

A method was conceived by which presence of the doubly-labeled PSCl_3 might be experimentally determined, quantitatively as well as qualitatively. It involved the assumption that in ten half-lives nearly all of an activity would have decayed. Actually $1/1024$, or a little less than 0.01 per cent, would remain but if the initial activity was not too high only a negligible amount would be present in a counting aliquot. If counting were continued until 143 days after the sample was removed from the reactor all P^{32} activity, for counting purposes, would be gone and the only labeled PSCl_3 species left, if no exchanges had occurred, would be $\text{PS}^{35}\text{Cl}_3$. One could calculate the amount of $\text{PS}^{35}\text{Cl}_3$ present at time of first assay by the relationship

$$A_0 = A/e^{-\lambda t}$$

where A_0 would be the activity at time of first assay, A was the activity measured at the 143 day time, λ was the characteristic decay constant and t was the time lapse between time of initial assay and the 143 day time expressed in units determined by the λ value.

The total S^{35} activity at time of initial assay was known and subtraction of the value just found for the S^{35} incorporated in the singly-labeled molecule would give the value of S^{35} activity in the doubly-labeled variety. Since a one-to-one relationship of S^{35} to P^{32} existed in the doubly-labeled molecule, the activity of P^{32} in the doubly-labeled

molecules would now be known. By subtracting the value of P^{32} activity in doubly-labeled $PSCl_3$ from the total value of P^{32} activity measured at time of first assay, the value of P^{32} activity in the singly-labeled variety could be obtained.

The same results could be shown graphically by plotting values of activity to the 143 day point and extending a line back with an 87.1 day half-life. This line would show S^{35} activity in $PS^{35}Cl_3$ at every point and could be compared with a plot of total S^{35} activity measured at each point to determine $P^{32}S^{35}Cl_3$ activity.

It should be mentioned that repurification and fresh sampling would be necessary at each time of assay or else labeled fragments of broken molecules would give indications identical to that of singly-labeled molecules.

Experimental Results

The results of fractional distillation of a 4.9 ml. sample of irradiated $PSCl_3$, to which were added 3 ml. PCl_3 , 2 ml. $PSCl_3$ and 2 ml. S_2Cl_2 as carriers, are shown in Table 3.

Table 3. Distillation of irradiated PSCl_3 with added carriers, Series II.

Fraction	Volume ^a	Distillation Temp.	$\text{P}^{32}/\text{S}^{35}$ ratio ^{b,c}
A	2.0 ml.	to 76° C.	7.66
B	1.2	76-120 ^{od}	17.77
C	5.3	120-128°	2.12
D	2.7	128-128°	1.77
Residue	0.6	-----	0.73

a. volumes measured by calibrated receiving flasks, residue volume obtained by difference.

b. average of three experimental values.

c. $\text{P}^{32}/\text{S}^{35}$ ratio of irradiated material was 1.03.

d. All but final drop collected at 76°.

Although complete separations could not be expected in a single distillation, the boiling points, $\text{P}^{32}/\text{S}^{35}$ ratios and volumes indicated that fractions A and B might contain P^{32}Cl_3 with some labeled PSCl_3 (singly and/or doubly-labeled).

The distillation temperatures, $\text{P}^{32}/\text{S}^{35}$ ratios and volumes of fractions C and D indicated the probability that these fractions were mostly composed of singly and/or doubly-labeled PSCl_3 . The data for the residue were less conclusive but indicated the probable presence of PSCl_3 , a lot of S^{35} activity and possibly PCl_5 . It was felt that this residue probably contained all these as well as S_2Cl_2 and some polymeric

structures induced at distillation temperatures but accidental spillage prevented an investigation of it.

Fractions A and B were combined, 2 ml. of PCl_3 were added as carrier material and another distillation was performed. The average p^{32}/s^{35} value then obtained in a fraction that distilled at $74-75^\circ \text{C}$ was 38.35. Fractions A and B were considered to be mostly PCl_3 . No indications of labeled PCl_3 were found in redistilled fractions of C and D, which were combined before the redistillations. No indications for compounds other than PSCl_3 were found in successive distillations of the C and D fractions. The radioactive portion of fractions C and D were singly and/or doubly-labeled PSCl_3 molecules.

The results of an earlier distillation of a 4.9 ml. sample of irradiated PSCl_3 , using 3 ml. PSCl_3 carrier and 2 ml. PCl_3 carrier are shown in Table 4.

Table 4. Distillation of irradiated PSCl_3 with added carriers, Series I.

Fraction	: Volume	: Distillation Temp.	: p^{32}/s^{35} ratio
A'	1.2 ml.	90- 96°C	5.14
B'	2.2 ml.	96-120°	3.77
C'	5.2 ml.	120-124°	3.17
Residue	1.3 ml.	-----	2.87

The poor separations indicated in this distillation led to the later use of a Raschig-ring packed distillation head, wrapped in asbestos mat for better heat regulation. Redistillation of fraction A' with 2 ml. PCl_3 and 1 ml. PSCl_3 as added carriers gave 2 ml. of impure PCl_3 , distilling at 72-80°C and having a $\text{P}^{32}/\text{S}^{35}$ ratio of 11.45.

Attention was turned to fraction C' which appeared to be nearly pure PSCl_3 . A counting aliquot was withdrawn and a counting sample prepared from it. The results are shown in Plate III. The curves indicated the presence of both P^{32} and S^{35} but did not prove or disprove the presence of doubly-labeled molecules since nothing was done to separate labeled fragments, and a sulfur³⁵ labeled fragment would give the same indications as a sulfur³⁵ labeled PSCl_3 molecule.

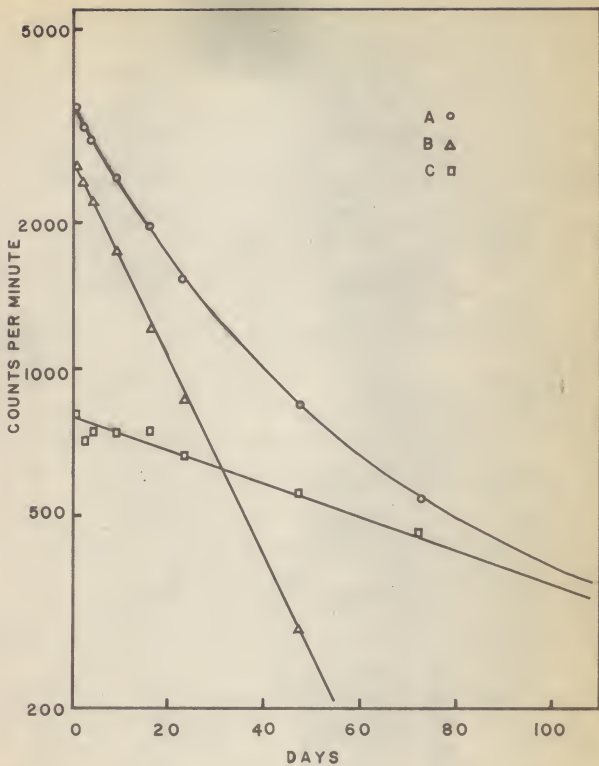
In order to determine whether or not doubly-labeled PSCl_3 molecules were present, a series of consecutive distillations were performed on fraction C' to remove any P^{32} or S^{35} labeled fragments formed by breakup of doubly-labeled molecules after decay of one or the other of the activities. The results obtained in assay were corrected for dilutions by added carriers and for variations in counting sample size. The corrected counting data as well as the results before correction are shown in Table 5.

EXPLANATION OF PLATE III

β^- Half-life Study, Labeled PSCl_3 Distillate C'

Curve A was obtained without absorbers and represents total activity. Curve B was obtained by multiplying readings obtained with a 34.5 mg/cm^2 absorber by 1.2 to correct for absorption of part of the P^{32} activity. The 14.3 day half-life is due to the P^{32} . Curve C is an 87.1 day half-life line drawn through points representing the differences in curves A and B. It shows the S^{35} activity present.

PLATE III



EXPLANATION OF PLATE IV

β^- Assay, Redistilled PSCl_3

Curve A was obtained without absorbers and represents the total activity at each point. Curve B was obtained by drawing a line through the corrected P^{32} activity at each point. Curve C was obtained by drawing a line through the corrected S^{35} activity at each point and is identical with the curve showing $\text{PS}^{35}\text{Cl}_3$ activities. No evidence was obtained for $\text{P}^{32}\text{S}^{35}\text{Cl}_3$.

PLATE IV

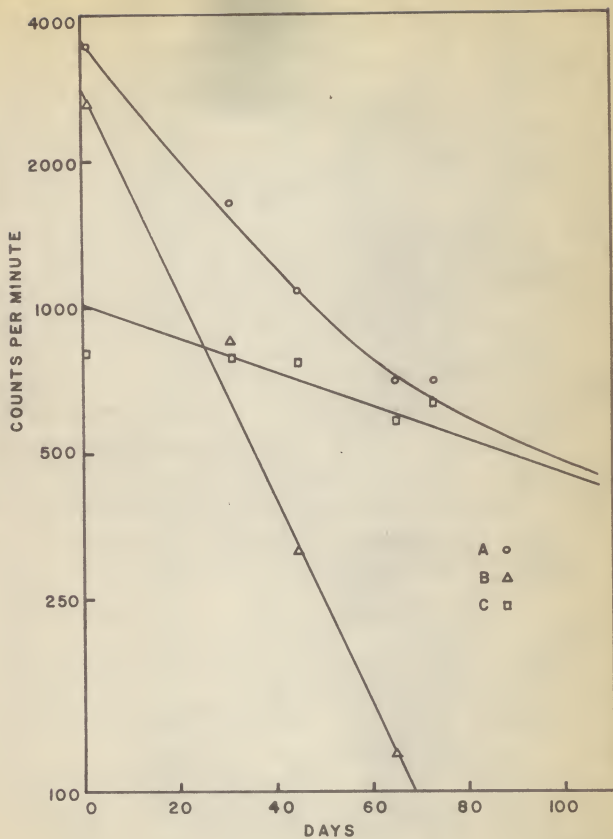


Table 5. Counting data, labeled PSCl_3 fraction C' after consecutive distillations.

Date	P ³² Activity*	Corrected P ³² Act.	S ³⁵ Activity	Corrected S ³⁵ Act.
12/12/53	2625.6	2625.6	827.4	827.4
1/11/54	2160.0	864.0	1959.0	783.6
1/25/54	434.4	312.8	1061.6	764.4
2/14/54	97.2	121.5	457.8	572.3
2/22/54	14.4	72.0	125.6	628.0

* all activities are expressed in counts/minute.

As discussed before, the presence of doubly-labeled PSCl_3 molecules would be indicated by a half-life curve of less than 14.3 days. Plate IV shows the curves obtained from the corrected data in Table 5. The absence of any indication of a half-life less than 14.3 days should be noted. No evidence for presence of doubly-labeled PSCl_3 molecules was obtained.

When the curves were extrapolated past 143 days, the composite curve A was identical with the S^{35} curve C. Since the method of continued distillations removed all labeled fragments, only $\text{PS}^{35}\text{Cl}_3$ molecules were present after the decay of all P^{32} (virtually complete at 143 days). When this line was extended back to the initial counting time, it fell

on top of curve C. Thus the S^{35} activity at each point could be ascribed to $PS^{35}Cl_3$ molecules and no S^{35} activity from $P^{32}S^{35}Cl_3$ was found. It was concluded that within the experimental errors involved in assay and volume measurements, no doubly-labeled $P^{32}S^{35}Cl_3$ molecules were formed in the irradiation. Thus, the $PSCl_3$ system appeared to be different than the PCl_3 system where Conn (9) found evidence for preferential formation of doubly-labeled $PSCl_3$ molecules.

Activity distributions were determined but because of incomplete separations obtained in single distillations the activity distributions calculated on the basis of first distillations were probably in error. These errors were reduced to some extent by further distillations. Corrections were made for dilution factors, geometry factors and decay of the radioactive nuclides between assays. Table 6 shows the average calculated per cents of P^{32} and S^{35} in the major fractions investigated in the two irradiated samples previously discussed.

Table 6. P^{32} and S^{35} distribution.

Fraction :	P^{32}		S^{35}	
	Series I	Series II	Series I	Series II
PCl_3	0.8 %	20.0 %	---	---
$PSCl_3$	58.43%	42.38%	60.62%	53.96%

These data represent the known per cents of the nuclides in the two compounds and may be in error if the separations were not complete as assumed. The P^{32} found in the PCl_3 fraction in Series I appeared very low and was another manifestation of the poor separations obtained before the use of a Raschig-ring packed distillation column.

P^{32} could be produced in three ways from $PSCl_3$, by $P^{31}(n,\gamma)P^{32}$, $S^{32}(n,p)P^{32}$ and $Cl^{35}(n,\alpha)P^{32}$. No direct indications were available as to the relative amounts produced in the three reactions. In an effort to obtain some knowledge along these lines, a comparison was made with the results of other irradiated compounds of phosphorus, sulfur and chlorine. These data were supplied by P. K. Conn.

For purposes of comparison it was necessary to adjust the data for the time intervals between removal of the samples from the pile and the actual assays. Corrections had to be made for the relative amounts of the three target nuclides in the specified compounds by taking into account the weights and isotopic abundances of the target elements. It was also necessary to correct for counting sample dilutions and counting geometries. When P^{32} activity was measured in the presence of S^{35} , corrections to zero absorber conditions were made. Table 7 shows the corrected data.

Table 7. Corrected data for comparisons of various phosphorus-sulfur-chlorine compounds.

Sample	:	Total P^{32} act.	:	Wt. P^{31}	:	Wt. S^{32}	:	Wt. Cl^{35}
4.9 ml $PSCl_3$		1.64×10^{10} c/min		1466 mg		1439 mg		3800 mg
4.9 ml $PSCl_3$		2.25×10^{10}		1466		1439		3800
1.9 ml PCl_3		8.04×10^9		679		---		1756
8.0 ml S_2Cl_2		8.05×10^9		---		6080		5346

Comparison of $PSCl_3$ with PCl_3 would give the amount of P^{32} formed in $PSCl_3$ by nuclear reactions of P^{31} and Cl^{35} . Subtraction of this value for P^{32} from the actual measured value of P^{32} would give the amount of P^{32} formed by the (n,p) reaction with S^{32} . The total P^{32} formed in the PCl_3 gave an activity value of 8.04×10^9 c/min. This was for 679 mg P^{31} and 1756 mg Cl^{35} . This was equivalent to 1.74×10^{10} c/min for the P^{32} formed by P^{31} and Cl^{35} in the $PSCl_3$ because a correction factor of 2.15 was applied to make the weights of P^{31} and Cl^{35} in the two compounds comparable. This value of 1.74×10^{10} c/min represented the P^{32} from P^{31} and Cl^{35} and subtraction of it from the total P^{32} value (average of the two values listed) gave $(1.95 \times 10^{10}$ c/min - 1.74×10^{10} c/min) or 2.1×10^9 c/min as the amount of P^{32} formed from S^{32} . This was 10.8 per cent of the total P^{32} .

Since the S^{32} produced 1.74×10^{10} c/min P^{32} for 1439 mg, the S^{32} in the S_2Cl_2 (8 ml sample) would produce (6080) ($1.74 \times 10^{10}/1439$) or 7.35×10^{10} c/min P^{32} activity. Subtraction of this value for P^{32} activity from the total P^{32} activity found present in the irradiated S_2Cl_2 should give the value of P^{32} activity from the $Cl^{35}(n,\alpha)P^{32}$ reaction. When this method was used it was found that total P^{32} activity observed in the irradiated S_2Cl_2 was less than that calculated from the $S^{32}(n,p)P^{32}$ reaction. It must be assumed that the S_2Cl_2 was not irradiated under conditions identical with those used for the PCl_3 and $PSCl_3$. It is probable that only 1 or 2 per cent of the P^{32} produced in S_2Cl_2 was found from $Cl^{35}(n,\alpha)P^{32}$ and since it was shown that 10.8 per cent was formed from $S^{32}(n,p)P^{32}$ it was concluded that about 88.2 per cent was formed from $P^{31}(n,\gamma)P^{32}$. These results should be compared to those shown in the appendix where P^{31} , S^{32} and Cl^{35} contributed 96.3 per cent, 2.3 per cent and 1.4 per cent of the P^{32} activity, respectively.

S^{35} could be produced in two ways from $PSCl_3$, by $S^{34}(n,\gamma)S^{35}$ and $Cl^{35}(n,p)S^{35}$. Table 8 shows corrected data necessary to compare the PCl_3 and $PSCl_3$ systems.

Table 8. Corrected data for comparison of PCl_3 and PSCl_3 systems.

Sample	Total S^{35} act.	Wt. S^{34}	Wt. Cl^{35}
1.9 ml PCl_3	6.22×10^9 c/min	---	1756 mg
4.9 ml PSCl_3	1.60×10^{10}	63.6 mg	3800
4.9 ml PSCl_3	1.83×10^{10}	63.6	3800

1756 mg Cl^{35} in the PCl_3 produced 6.22×10^9 c/min S^{35} activity so the 3800 mg Cl^{35} in the PSCl_3 would produce (6.22×10^9 c/min) (3800 mg/1756 mg) or 13.44×10^9 c/min S^{35} . The average total S^{35} in the PSCl_3 samples was 1.72×10^{10} c/min so that ($13.44 \times 10^9 / 17.2 \times 10^9$) (100) or 78.1 per cent of the total S^{35} would be produced from Cl^{35} and the remaining 21.9 per cent would be produced from S^{34} . These results, based on experimental measurements, do not agree well with the 97.4 per cent from Cl^{35} and 2.6 per cent from S^{34} calculated in the appendix.

Sulfur Exchange Experiments

Possible sulfur exchange was of interest, both at room temperatures and at the distillation temperatures used to separate product molecular species. One exchange system of interest was that of elemental sulfur with PSCl_3 . Three

investigations were made on inactive PSCl_3 , to which had been added elemental S^{35} with inactive sulfur as carrier material. Induction periods of 30 minutes and 10 hours at room temperatures were used for the first two trials and an 84 hour period in a water bath (average temperature 82°C.) was used in the final trial.

Following the induction periods the solutions were distilled at the boiling point of PSCl_3 , 125°C. Five fractions and a residue were collected for each. A record was kept of distillation times and temperatures. In no case was activity above normal background found present in the first four fractions. This was taken as evidence that no exchange had occurred to that point. For the three trials an average value of 1.0 per cent of the total S^{35} activity appeared in the last fraction distilled. This was attributed to mechanical carryover rather than exchange, inasmuch as the residue volumes were relatively small. Within the limits of error involved in such experiments it was decided that no exchange took place under the specified conditions.

SUMMARY AND CONCLUSIONS

Absorber and half-life studies indicated the formation of P^{32} and S^{35} . No evidence for other nuclides was found. It is possible that other nuclides may have been formed in the irradiation but decayed during the interval between removal from the reactor and receipt by these laboratories.

Distillation temperatures and radioactivities indicated the presence of labeled $P^{32}Cl_3$ and singly-labeled $P^{32}S_2Cl_3$ and $PS^{35}Cl_3$. An investigation of PS_2Cl_3 fractions gave no positive evidence for presence of the doubly-labeled $P^{32}S^{35}Cl_3$. Accidental spillage prevented an investigation of residues whose boiling points and radioactivities suggested the probable presence of labeled S_2Cl_2 , labeled elementary S^{35} and $P^{32}Cl_5$. The presence of dark, colloidal material in the residues led to the conjecture that polymerization of some type might have taken place during distillations but no positive identifications were made.

Comparisons were made between irradiated PS_2Cl_3 , PCl_3 and S_2Cl_2 . It was seen that irradiation of the S_2Cl_2 was not done under conditions identical with the others. On the basis of experimental evidence, the P^{32} activity in irradiated PS_2Cl_3 was produced in the following ways: 10.8 per cent from S^{32} - $(n,p)P^{32}$, about 1 per cent from $Cl^{35}(n,\gamma)P^{32}$ and about 88.2

per cent from $P^{31}(n,\gamma)P^{32}$. The S^{35} activity in $PSCl_3$ was produced in the following ways: 2.6 per cent from $S^{34}(n,\gamma)-S^{35}$ and 97.4 per cent from $Cl^{35}(n,p)S^{35}$. These results were not identical to those calculated on a theoretical basis (appendix) where 96.3 per cent of the total P^{32} activity produced in one gram of irradiated $PSCl_3$ would be from P^{31} , 2.3 per cent would be from S^{32} and 1.4 per cent would be from Cl^{35} while 97.4 per cent of the total S^{35} activity in the same sample would be from Cl^{35} and 2.6 per cent would be from S^{34} . Because of the inexact nature of available data, neither method gave more than useful approximations.

About 50 per cent of both the P^{32} and S^{35} activities were retained in $PSCl_3$ fractions. With a Raschig-ring packed distillation column for better separation it was determined that about 20 per cent of the P^{32} was present as $P^{32}Cl_3$.

No evidence was obtained for any thermal exchange between elemental S^{35} and inactive $PSCl_3$ in work involving induction periods at room temperatures and none was found when the induction period was 3.5 days at a temperature of $80^\circ C$.

No postulates as to reaction mechanisms can be made until more work is done on similar systems. The work indicated the need for better separation techniques and at this writing vacuum distillations, modified chromatographic techniques and solvent extraction processes are contemplated for future irradiations.

ACKNOWLEDGMENTS

The author wishes to express his gratitude to his major professor, Doctor R. E. Hein, for advice, encouragement and criticisms and to his colleague, Mr. P. K. Conn, for ready assistance in the laboratory.

APPENDIX

Table 9. Thermal Neutron Cross Sections.

Reaction	:	Cross Section	:	Reference
$P^{31}(n, \gamma)P^{32}$		$0.23 \times 10^{-24} \text{ cm}^2$		(36)
$P^{31}(n, p)Si^{31}$		0.074×10^{-24}		(33)
$S^{32}(n, p)P^{32}$		0.30×10^{-24}		(22)
$S^{34}(n, \gamma)S^{35}$		0.26×10^{-24}		(36)
$S^{36}(n, \gamma)S^{37}$		0.14×10^{-24}		(19)
$Cl^{35}(n, p)S^{35}$		0.169×10^{-24}		(36)
$Cl^{35}(n, \alpha)P^{32}$		0.017×10^{-24}		(34)
$Cl^{37}(n, \gamma)Cl^{38}$		0.56×10^{-24}		(36)

Theoretical Activity Calculations

Using cross section values from the above table, appropriate neutron fluxes and isotopic abundances, the per cents of total P^{32} activity that would be formed in a one week irradiation of a one gram sample of pure $PSCl_3$ were determined for the following reactions: $P^{31}(n, \gamma)P^{32}$; $Cl^{35}(n, \alpha)P^{32}$ and $S^{32}(n, p)P^{32}$. In a one gram sample of $PSCl_3$ there would be 0.183 grams of P^{31} , 0.179 grams of S^{32} and 0.474 grams of Cl^{35} . Neutron fluxes of sufficient energies to initiate the reactions were ascertained by private communication with Oak Ridge

National Laboratories.

The general formula for this type problem is

$$A = \sigma f N (1 - e^{-\lambda t})$$

where σ is the cross section, f is the incident neutron flux, N is the number of target nuclides originally present (generally large and assumed constant for the irradiation), λ is the characteristic decay constant and t is the irradiation time.

Substitution of the proper values for the $P^{31}(n,\gamma)P^{32}$ reaction gave

$$A(\text{dis/sec}) = [0.23 \times 10^{-24} \text{ cm}^2] [5 \times 10^{11} \text{ n/cm}^2/\text{sec}]$$

$$\left[\left(\frac{0.183 \text{ gm}}{31 \text{ gm/mole}} \right) 6.02 \times 10^{23} \text{ atoms/mole} \right]$$

$$\left[1 - e^{-\{(.693)/14.3 \text{ days}\} (7 \text{ days})} \right]$$

or a value for A of 117.6×10^6 dis/sec.

Similar use of the formula for the $Cl^{35}(n,\gamma)P^{32}$ reaction, where the neutron flux of necessary energy was 4.3×10^{10} n/cm²/sec, gave a value for A of 1.73×10^6 dis/sec. In like manner, for the $S^{32}(n,p)P^{32}$ reaction, where the flux was 1.2×10^{10} n/cm²/sec, the value of A was determined to be 2.85×10^6 dis/sec. A comparison of the three values of A showed that $(117.6/122.18)$ (100) or 96.3 per cent of the P^{32} would be from P^{31} , $(1.73/122.18)$ (100) or 1.4 per cent would be from Cl^{35} and $(2.85/122.18)$ (100) or 2.3 per cent would be formed from S^{32} .

By the same method it was calculated that 9.94×10^5

dis/sec would be the activity of S^{35} activity produced from $S^{34}(n,\gamma)S^{35}$ and 372.75×10^5 dis/sec would be the S^{35} activity produced from $Cl^{35}(n,p)S^{35}$. Thus $(9.94/382.69) (100)$ or 2.6 per cent of the S^{35} would be formed from S^{34} and $(372.75/382.69) (100)$ or 97.4 per cent of the S^{35} would be formed from Cl^{35} .

It should be noted that total P^{32} activity per gram of pure $PSCl_3$ calculated this way was 1.22×10^8 dis/sec and the total S^{35} activity was 3.83×10^7 dis/sec.

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AN INVESTIGATION OF NEUTRON-IRRADIATED
THIOPHOSPHORYL CHLORIDE

by

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A. B., Kansas State Teachers College
Pittsburg, Kansas, 1951

AN ABSTRACT OF A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

1955

PSCl_3 samples, subjected to fluxes of thermal neutrons for one week periods, were examined for induced radioactivities, chemical composition and activity distributions.

Only two radioactive nuclides were found in the neutron-irradiated PSCl_3 . These nuclides were identified by two methods. Absorption of the beta rays in calibrated aluminum absorbers gave maximum beta energies of 1.7 mev and 0.169 mev and subsequent half-life studies gave values of 14.3 days and 87 days for the half-lives of the high and low energy beta emitters, respectively. On the basis of these studies, the two nuclides were identified as P^{32} and S^{35} .

Approximately 50 per cent of the total P^{32} and S^{35} activities for each sample were found present in the PSCl_3 fractions obtained in fractional distillations of the samples at atmospheric pressure. Twenty per cent of the P^{32} was found in PCl_3 fractions when careful distillations were performed, using a Raschig-ring packed distillation column. Accidental spillage prevented proper investigation of the residues but observed activities, coloration and distillation temperatures indicated the probable presence of labeled PCl_5 , S_2Cl_2 and elemental sulfur and the possible presence of polymers produced at the distillation temperatures.

Since P. K. Conn tentatively identified the doubly-labeled $\text{P}^{32}\text{S}^{35}\text{Cl}_3$ species in neutron-irradiated PCl_3 , a search was made for that molecular species in the PSCl_3 . No evidence was found

for the presence of the doubly-labeled compound in neutron-irradiated PSCl_3 .

Comparison of neutron-irradiated samples of PSCl_3 , PCl_3 and S_2Cl_2 showed that about 88.2 per cent of the total P^{32} activity produced in the PSCl_3 samples was produced by the $\text{P}^{31}(\text{n},\gamma)\text{P}^{32}$ reaction, about 10.8 per cent by $\text{S}^{32}(\text{n},\text{p})\text{P}^{32}$ and about 1 per cent by $\text{Cl}^{35}(\text{n},\alpha)\text{P}^{32}$. Attempts at comparisons with the S_2Cl_2 samples indicated that their irradiations were at conditions not identical with those used in the PSCl_3 and PCl_3 . The comparisons also indicated that 78.1 per cent of the total S^{35} produced in irradiated PSCl_3 was produced by the $\text{Cl}^{35}(\text{n},\text{p})\text{S}^{35}$ reaction and 21.9 per cent by the $\text{S}^{34}(\text{n},\gamma)\text{S}^{35}$. These experimental results did not compare well with values calculated for a hypothetical one week irradiation of a one gram sample of pure PSCl_3 where 96.3 per cent of the total P^{32} would be from P^{31} , 2.3 per cent from S^{32} and 1.4 per cent from Cl^{35} and where 97.4 per cent of the total S^{35} would be produced from Cl^{35} and 2.6 per cent would be from S^{34} .

Three investigations of possible exchange of S^{35} with the sulfur in PSCl_3 were made, two with induction periods at room temperatures and one with an 84 hour induction period at an average temperature of 82°C . Investigation of distillates at the boiling point of PSCl_3 (125°C) gave negative results and it was concluded that no exchange occurred under these conditions.

No attempts at mechanism postulations are made at this time because further investigation of this system and investigations of similar systems must be made.

