inductive effect between the bond moment of C=O and that of C–Cl and assuming that these bonds are in the same plane for this form.[10] This value is the same as that estimated by Mizushima, *et al.*,[11] for the more stable rotational isomer of α-chloroacetone. The moment μ_a is similarly estimated to be 2.5 *D* which is nearly the same as that estimated by Kumler, *et al.*,[12] for the (a)-form. The value of a^3 was determined to be 4.54 × 10^{-23} cc. by the measurement of density at 23° (d^{23}_4 1.158). The dielectric constant of this substance was measured to be 26.8 at the same temperature. By use of these values the values of $\Delta(\Delta E)$ were calculated. The results are shown in Table V together with the energy differences determined by the intensity measurements. The value of $\Delta(\Delta E)$ and those of ΔE have the same meaning, because the energy difference ΔE in the vapor is nearly zero.

TABLE V

ENERGY DIFFERENCE BETWEEN THE TWO FORMS

State	Dielectric constant	$-\Delta E$, kcal./mole	
		Obsd.	Calcd.
Pure liq.	26.8	1.11	1.0
Pyridine soln.	12.5	0.94	0.94
CS_2 soln.	2.63	0.81	0.55

The contour of the broad band near 1730 cm.$^{-1}$ was investigated for the various states by use of the CaF_2 prism. Because of a complicated feature of the contour, it seems difficult to divide the broad band into the band of the (e)-form and that of the (a)-form.

The band at 714 cm.$^{-1}$ may be assigned to the C–Cl stretching vibration for the (e)-form and the band at 699 cm.$^{-1}$ to that for the (a)-form. The assignments are in agreement with the rule[13] reported by one of the authors that for the C–X (X = halogen) stretching frequencies of various cyclohexane derivatives the frequency of the C–X bond having the X atom in the (e)-orientation is higher than that of the bond having the X atom in the (a)-orientation. According to Jones, *et al.*,[14] the band at 1430 cm.$^{-1}$ may be assigned to the scissoring vibration of the α-methylene group next to the carbonyl group.

By use of the moments, μ_e and μ_a, estimated for the two isomers and of the energy difference ΔE determined by the intensity measurements the dipole moment μ can be calculated by the formula

$$\mu = \{(r\mu_a^2 + \mu_e^2)/(1 + r)\}^{1/2}$$

where *r* is the abundance ratio of two isomers and is given approximately as

$$r = \exp(-\Delta E/RT)$$

The calculated value of 2.3 *D* is in good agreement with the observed value listed in Table III. In agreement with the results obtained by studying the infrared spectra, the observed value of the dipole moment also is evaluated by considering only the equilibrium of the (e)- and the (a)-form without assuming the coexistence of any other form, such as a flexible form assumed by Kumler, *et al.*[12]

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[10] This assumption seems to be reasonable when taking account of the structure of α-methylcyclohexanone determined by C. Romers (*Rec. trav. chim.*, **75**, 956 (1956)) with the aid of electron diffraction.

[11] S. Mizushima, T. Shimanouchi, T. Miyazawa, I. Ichishima, K. Kuratani, I. Nakagawa and N. Shido, *J. Chem. Phys.*, **21**, 815 (1953).

[12] W. D. Kumler and A. C. Huitric, THIS JOURNAL, **78**, 3369 (1956).

[13] K. Kozima, *Bull. Tokyo Inst. Tech.*, 1 (1952) (in Japanese).

[14] R. N. Jones and A. R. H. Cole, THIS JOURNAL, **74**, 5648 (1952).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, KANSAS STATE UNIVERSITY OF AGRICULTURE AND APPLIED SCIENCE]

Neutron and γ-Irradiation of Phosphorus Trichloride[1]

BY D. W. SETSER, H. C. MOSER AND R. E. HEIN

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Samples of liquid phosphorus trichloride were reactor irradiated for varying lengths of time, and the yield of P^{32}-labeled PCl_3 was measured. The percentage of the P^{32} in combination as $P^{32}Cl_3$ changed from 60 to 90% with increasing irradiation time. A radiation induced oxidation of radioactive P_2Cl_4 to form PCl_3 has been postulated to explain the changing distribution of P^{32}. Two labeled products, $P^{32}OCl_3$ and $P^{32}Cl_3$, were identified in reactor irradiated $POCl_3$. The relative yield of $P^{32}OCl_3$ was also found to increase with irradiation time.

Introduction

The present study was undertaken to investigate the chemical effects accompanying $P^{31}(n,\gamma)P^{32}$ reactions in PCl_3 and to determine what influence the γ-ray dosage has upon the distribution of products containing P^{32}. When samples of PCl_3 are reactor irradiated, they are subjected to a large γ-ray flux because of contributions from both external and internal sources. This system is also somewhat unusual in that recoil atoms from nuclear reactions should thermalize rapidly because all of the atoms have nearly equal mass.

Phosphorus atoms of PCl_3 which capture neutrons are very likely given enough recoil energy to break one or more of their bonds. The initial γ-ray emitted by a phosphorus atom following neutron capture is 3.5 Mev. or greater[2] which produces a recoil energy of at least 205 e.v. This is sufficient energy to break the chemical bonds in PCl_3 (3.4 e.v.) unless successive emission of γ-rays cancels the recoil energy.

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[1] Work performed under contract No. AT (11-1)-584 with the U. S. Atomic Energy Commission. Taken in part from a thesis submitted by Donald W. Setser in partial fulfillment of the requirements for the degree of Master of Science, January, 1958.

[2] B. B. Kinsey, G. A. Bartholomew and W. H. Walker, *Phys. Rev.*, **85**, 1012 (1952).

Results of a previous study[3] gave indication that 88% of the total P^{32} was either re-formed or retained in chemical combination as $P^{32}Cl_3$ regardless of total neutron dosage, irradiation temperature or phase (liquid or gas). Shorter irradiation times were used in the present study, and lower percentages of P^{32} in combination as $P^{32}Cl_3$ were found. If extensive bond ruptures occur in PCl_3 leading to the formation of other phosphorus–chlorine compounds, the latter must be converted to PCl_3 by a radiation effect.

Experimental

Reagents.—Reagent grade (Mallinckrodt) PCl_3 was quadruply distilled through a six inch column packed with glass helices. Samples for irradiations were prepared from this by distilling the PCl_3 at reduced pressure in the presence of helium into 1.6 × 4 cm. quartz ampoules cooled in a Dry Ice-acetone bath. The desired volume of PCl_3 then was sealed in the ampoule at a pressure of about 250 μ. Reagents for carriers were prepared by doubly distilling reagent grade PCl_3 (Mallinckrodt) and $POCl_3$ (Merck); $PSCl_3$ carrier was synthesized[4] and redistilled, and reagent grade decane (Matheson, Coleman and Bell) was used without further treatment for some samples. In the later work the decane was shaken with concentrated H_2SO_4 for 20 hr., washed with water and redistilled.

Irradiations.—Samples were irradiated in the X-10 Graphite Reactor at the Oak Ridge National Laboratory. Two positions were used depending upon the requested neutron dosage. One position had a reported thermal flux of 1×10^{11} n. cm.$^{-2}$ sec.$^{-1}$ and γ-intensity of 5.6×10^4 r. hr.$^{-1}$; the other position had a flux of 6×10^{11} n. cm.$^{-2}$ sec.$^{-1}$ and γ-intensity of 1.55×10^7 r. hr.$^{-1}$. The average temperature was reported as 50°. γ-Irradiations were done in the Oak Ridge facility, which had an intensity of about 10^6 r. hr.$^{-1}$.

Separations.—Irradiated samples were opened using the procedure of Conn and Hein.[3] Carriers (PCl_3, $POCl_3$, $PSCl_3$ and decane) were added, and the mixture was separated by distillation using a jacketed, 3 ft. × 1 in. column packed with glass helices. Aliquots were removed prior to distillation for P^{32} radioassay. One-ml. fractions of the phosphorus compounds were collected from the distillation column; the decane remained in the distillation pot and served as a hold-back carrier for high boiling products. Results of a representative distillation are given in Fig. 1. In this distillation 98% of the PCl_3 was recovered from the mixture; the separations of the other carriers were not as efficient.

Some distillations were carried out at reduced pressure to effect separations at lower temperatures, and the maximum distillation pot temperatures were about 60° in these distillations. Only PCl_3 and decane carriers were used because of the difficulty in separating PCl_3, $POCl_3$ and $PSCl_3$ at reduced pressures.

Counting Technique.—Counting data were obtained using a dipping counter assembly. The Tracerlab TGC 5 Geiger counter used had a wall thickness of 30 mg. cm.$^{-2}$ which was sufficient to absorb the soft β-particles from S^{35}. With water as the counting liquid, the counter assembly had an efficiency of 10% for P^{32} radioactivity.

Counting samples were prepared by mixing aliquots from the distillation fractions with enough xylene to give total volumes of 15 ml. The counter assembly was rinsed and a background reading was taken between each counting sample.

Results

Neutron Irradiations. (1).—Results of distillations of the irradiated PCl_3 samples are summarized in Table I in order of increasing P^{32} concentration. Experimental measurements of total P^{32} radioactivity were used to calculate the concentrations of P^{32} present at the time of removal from the reactor. These quantities are proportional to the neutron dosages received by the samples and are listed in the second column. Percentages recorded in the sixth column are estimates of additional amounts of activity which were carried by the final PCl_3 fractions in distillations at atmospheric pressure. These peaks were found for the short-time irradiations only, and Fig. 2 shows results of representative short and long-time irradiations. The peak, which is shown in the curve for sample F, occurred as the pot temperature approached 120°. Sample D was divided for analysis; one part, designated D, was distilled at atmospheric pressure, and the other, D′, was distilled at reduced pressure. Sample A was also separated by distillation at reduced pressure.

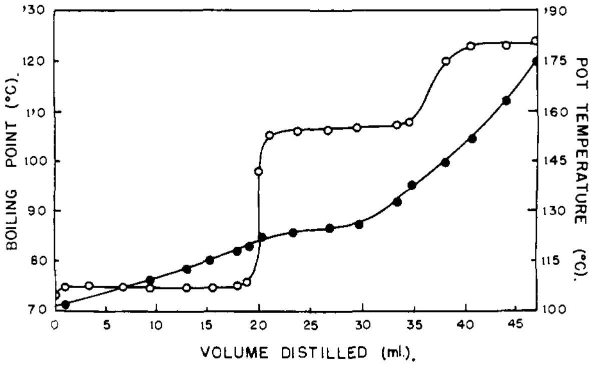

Fig. 1.—Distillation curve for the separation of 20 ml. of PCl_3, 13.5 ml. of $POCl_3$, 15.3 ml. of $PSCl_3$ and 15 ml. of decane: ○, head temperatures; ●, distillation pot temperatures.

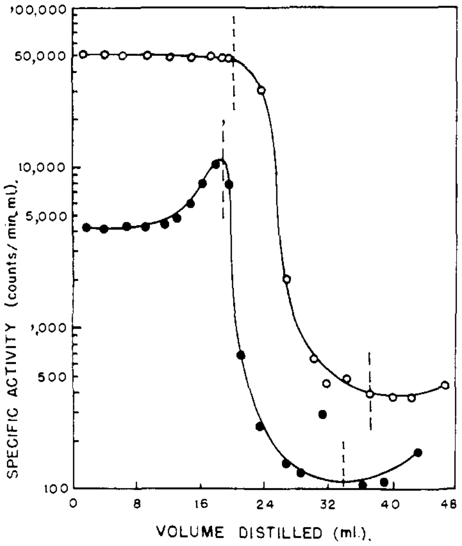

Fig. 2.—Specific activities of fractions from distillations of samples F and I. The first dotted line shows the transition from PCl_3 carrier to $POCl_3$ carrier; the second shows the transition from $POCl_3$ to $PSCl_3$: ●, sample F; ○, sample I.

Figure 3 is a plot of the variation of the % retention with the square root of the number of P^{32} atoms ml.$^{-1}$. The square root of the latter was used in order to contract the scale. The standard deviation indicated at each point was calculated from the results of the specific activity measurements.

(2).—Two samples of $POCl_3$ were irradiated. Experimental procedures were identical to those

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[3] R. K. Conn and R. E. Hein, THIS JOURNAL, **79**, 60 (1957).

[4] R. Knotz, *Osterr. Chem. Ztg.*, **50**, 128 (1949).

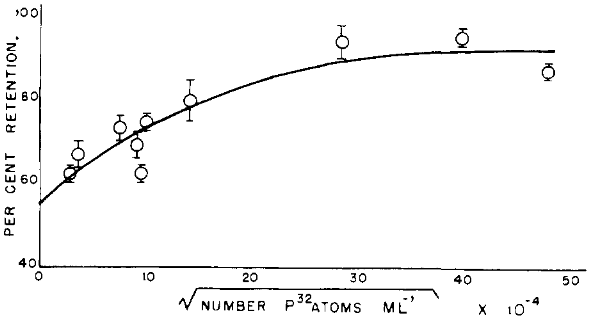

Fig. 3.—Percentage P^{32} in combination as $P^{32}Cl_3$ (% retention) following reactor irradiation of PCl_3.

used for the PCl_3 samples. One sample contained 1.6×10^{10} P^{32} atoms ml.$^{-1}$ and 45% of the P^{32} was carried by PCl_3, 29% by $POCl_3$, 4% by $PSCl_3$ and 14% remained in the decane; the other sample contained 1.3×10^{11} P^{32} atoms ml.$^{-1}$ and 32% of the P^{32} was carried by PCl_3, 45% by $POCl_3$, 2% by $PSCl_3$ and 18% remained in the decane. For both samples, equal specific activities were found for fractions collected while PCl_3 or $POCl_3$ was distilling.

Table I

Distribution of P^{32} in Reactor Irradiated PCl_3

Sample	No. of P^{32} atoms ml.$^{-1}$	% Retention[a]	% in $PSCl_3$	% in Decane	% in Peak
A[b]	7.58×10^8	62.2 ± 2	. .	29.0	0
B	1.21×10^9	67.2 ± 3	1.0	19.4	7
C[c]	5.95×10^9	73.6 ± 3	0.9	13.0	
D	8.25×10^9	69.4 ± 3	0.7	14.4	16
D′[b]	8.25×10^9	65.5	. .	28.8	0
E[d]	8.51×10^9	98.0 ± 2	0.0	0.67	0
F	9.44×10^9	62.4 ± 2	1.0	12.7	17
G	9.72×10^9	75.0 ± 2	0.7	14.2	2
H	1.98×10^{10}	79.7 ± 5	1.0	11.4	0
I	7.99×10^{10}	94.1 ± 4	0.4	1.0	0
J	1.57×10^{11}	95.4 ± 2	0.8	2.0	0
K	2.29×10^{11}	87.3 ± 2	2.0	3.1	0

[a] Per cent. retention is defined as the per cent. of the total P^{32} radioactivity which distilled with the PCl_3 exclusive of the additional activity found in the peaks. [b] Distilled at reduced pressure. [c] Sample C had some radioactivity in the peak but the data were not complete enough to analyze. [d] Sample E received a γ-ray dosage of 2.9×10^7 roentgens in addition to the pile irradiation.

(**3**).—A value of 3×10^{10} Mev. sec.$^{-1}$ was calculated as the approximate energy deposited in an 8-ml. cylindrical (1.6 cm. × 4 cm.) sample of PCl_3 irradiated for one minute at a thermal flux of 1×10^{11} n. cm.$^{-2}$ sec.$^{-1}$ and γ-intensity of 5.6×10^4 r. hr.$^{-1}$. The amount of P^{32} found in sample B (irradiated for 60 sec. at 1×10^{11} n. cm.$^{-2}$sec.$^{-1}$) was used to calculate the number of $P^{31}(n,\gamma)P^{32}$ reactions and yields for neutron induced reactions in chlorine. It was assumed that the ratio of the yields for particular reactions was the same as the ratio of their macroscopic cross sections. The γ-ray energy for each process was taken as the quotient of the Q-value and 2.5, the approximate number of γ-rays emitted per neutron capture.[5] The largest contribution to the energy absorbed was from the attenuation of internal (67%) and external (32%) γ-rays.

γ-Irradiations. (**1**).—Following neutron irradiation, sample E (Table I) was subjected to an additional γ-irradiation of 2.9×10^7 r. For comparison, sample G was given a similar reactor irradiation but was not subjected to any further γ-irradiation.

(**2**).—A 6.8-ml. aliquot of a 2.3% solution of P^{32}-labeled white phosphorus in PCl_3 was irradiated with γ-rays of intensity 2.6×10^6 r. hr.$^{-1}$ for a period of 13.8 hr. The sample was analyzed 24 days after the solution was prepared. Another sample was used as a control without irradiation and was analyzed 22 days after preparation. Carriers (PCl_3, $POCl_3$, $PSCl_3$ and decane) were added to both samples and the resultant mixtures separated by fractional distillation at atmospheric pressure. The sample which was γ-irradiated had 13.5% of the P^{32} carried by PCl_3, none by $POCl_3$, 2% by $PSCl_3$ and the remainder was retained in the decane; the other sample had 3% of the P^{32} carried by PCl_3, none by $POCl_3$ or $PSCl_3$ and the remainder was retained in the decane. Equal specific activities were found for the PCl_3 fractions from a given sample. The γ-rays converted some of the dissolved phosphorus to red phosphorus and the latter precipitated; therefore, the solution was not completely homogeneous during the latter part of the irradiation. A fraction exchange of 0.12, corrected for exchange that occurred in the control sample, was attributed to the γ-irradiation. This fraction corresponds to an exchange of 5.2×10^{19} phosphorus atoms per gram of solution. The energy absorbed by the sample was calculated to be 2.3×10^{15} Mev. g.$^{-1}$ indicating that about 2.3 phosphorus atoms exchanged per 100 ev. absorbed.

Discussion

Species Containing P^{32}.—Equal specific activities were found for all PCl_3 fractions from the reduced pressure distillations of short-time irradiated samples and from atmospheric distillations of long-time irradiations. Fractions of PCl_3 which were collected in the constant specific activity region probably contained only $P^{32}Cl_3$ as the species with P^{32}. Those fractions in the peak region which had increased specific activities contained either species in addition to $P^{32}Cl_3$ or the enrichment of $P^{32}Cl_3$ resulted from a reaction in the distillation pot.

The specific activity of each successive $POCl_3$ fraction was less than that of the preceding fraction which indicates that this radioactivity was due to $P^{32}Cl_3$ which was washed from the distillation head by the liquid $POCl_3$. The specific activity increased in successive $PSCl_3$ fractions implying that a radioactive product with a b.p. of about 125° was present. However, it was a very small fraction of the total P^{32} radioactivity.

The identity of the species retained in the decane was not established definitely. A small amount of this activity probably was due to hydrolysis of $P^{32}Cl_3$ during post-irradiation handling procedures. The activity was not removed when PCl_5 carrier was added, reduced to PCl_3 with white phosphorus and distilled. Neither was it carried by P_4S_3, P_4S_{10} or P_4S_7 when these compounds were added, chlorinated and distilled. In the samples (A, D′,

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[5] C. O. Muehlhause, *Phys. Rev.*, **79**, 277 (1950).

F, K) to which treated decane was added as carrier, the activity retained in the decane was extracted with water. On other samples about 70% of this activity was not extracted by aqueous solutions (acidic, neutral or basic) and was not chlorinated by PCl_5 to make it water extractable. The change probably was due to a reaction of impurities in the decane with the high boiling component and not with $P^{32}Cl_3$. Reaction with $P^{32}Cl_3$ could not account for any sizable percentage of P^{32}. A solution of reagent grade decane, $POCl_3$, $PSCl_3$ and $P^{32}Cl_3$ was distilled and all of the radioactivity was removed leaving a decane residue which was essentially free of P^{32}.

Assuming that the samples which were irradiated contained only the elements phosphorus and chlorine, the P^{32} must then have been present as elemental phosphorus and/or phosphorus–chlorine compounds. In addition to the well known phosphorus halides PCl_3 and PCl_5, Besson and Fournier[6] have reported a synthesis of P_2Cl_4 (b.p. 180°, f.p. −28°). They reported that P_2Cl_4 decomposed upon heating to give elemental phosphorus and PCl_3. The formation of P_2Cl_4 during the recoil process might explain the activity in the peak and that retained in the decane. As the temperature of the distillation pot is raised, the P_2Cl_4 containing P^{32} should decompose yielding high specific activity PCl_3 and elemental phosphorus. The $P^{32}Cl_3$ would then distill with the last fractions of PCl_3, and the elemental phosphorus would remain in the distillation pot. Attempts to synthesize P_2Cl_4 were unsuccessful, but it is the only known phosphorus halide with the required properties.

If $P^{32}Cl_5$ was formed during the irradiations, the P^{32} would have exchanged between this compound and PCl_3.[7] The results of this study did not give indication of an exchange reaction. The length of time before analysis did not significantly affect the amount of radioactivity that was distilled with the PCl_3 fractions, and radioactive PCl_3 was not found in the distillation pots. Any exchange must have taken place in the reactor or following the irradiation before analysis.

Radiation Effects.—Extrapolation of the data in Fig. 3 indicates that 50 to 60% of the P^{32} atoms are initially in combination as $P^{32}Cl_3$. In samples irradiated for longer than 5 min. at a flux of 6×10^{11} n. cm.$^{-2}$ sec.$^{-1}$, about 90% of the P^{32} is present as $P^{32}Cl_3$. These data suggest that some of the initial products which contain P^{32} are converted to $P^{32}Cl_3$ by γ-ray induced radiolysis during irradiation. Further indication of this can be noted in the results of samples G and E which were given similar reactor irradiations. The additional γ-irradiation given sample E brought about an increase in retention from 75 to 98%.

If a phosphorus halide such as P_2Cl_4 is formed in the recoil process, it should be converted to PCl_3 if oxidizing agents are produced by the radiolysis of PCl_3. The results of the γ-ray induced exchange of white phosphorus with PCl_3 substantiate the presence of oxidizing agents in irradiated PCl_3. The number of phosphorus atoms that could be oxidized by the absorption of 3×10^{10} Mev. sec.$^{-1}$ is approximately 7×10^{14} atoms sec.$^{-1}$, and this is much greater than the rate of production of P^{32} atoms. Of course the probability for oxidation of products containing P^{32} is small unless a stable radiolysis product is formed,[8] but the formation of PCl_5 which is both stable and a good oxidizing agent seems plausible. At the same time a reduced phosphorus halide must be produced also, and the concentration of this and PCl_5 should reach a steady state if the irradiation time is long enough.

The marked radiation effect in the PCl_3 system explains why Conn and Hein[3] observed a constant per cent. retention in their study. Their samples were irradiated sufficiently long so that only $P^{32}Cl_3$ was present as a major product.

Recoil Effects.—A reduced percentage of P^{32} was found combined as the subject compound in the short-time irradiations of PCl_3 or $POCl_3$. Evidently, chemical changes accompany a rather large fraction of the $P^{31}(n,\gamma)P^{32}$ reactions in these compounds.

The distribution of products in reactor irradiated $POCl_3$ appears to be influenced by γ-radiation similar to PCl_3, and the net effect is the conversion of $P^{32}Cl_3$ to $P^{32}OCl_3$. There is insufficient data at present to estimate the extent of this conversion in either of the two irradiations. If the change due to γ-radiation can be estimated and subtracted, the ratio of $P^{32}Cl_3$ to $P^{32}OCl_3$ should reflect the probability of their formation following neutron capture and hence indicate the extent of bond breaking accompanying these nuclear reactions. Further work is in progress in the study of the $POCl_3$ system.

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[6] A. Besson and L. Fournier, *Compt. rend.*, **150**, 102 (1910).

[7] W. E. Becker and R. E. Johnson, THIS JOURNAL, **79**, 5157 (1957).

[8] C. J. Chien and J. E. Willard, *ibid.*, **77**, 3441 (1955).