

762. *Thermal-neutron Capture in Gaseous and Liquid Phosphines. Part III.¹ Mechanism of Formation of Phosphorus-32-labelled Recoil Products.*

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In the radiative thermal-neutron capture in gas mixtures containing phosphine and methane, about $50 \pm 10\%$ of the resulting phosphorus-32 was in the form of phosphine. This retention of [³²P]phosphine was not decreased by addition of various rare gases which should act as moderators for "hot" phosphorus atoms. Addition of compounds which could possibly scavenge thermal phosphorus atoms had no effect on the retention. This independence of yield on reaction conditions seems to indicate that "hot" phosphorus atoms are unable to form stable products, and that phosphine itself (the target material) is a very efficient scavenger for thermal phosphorus atoms.

In previous studies¹⁻³ the distribution of phosphorus-32-containing products, following thermal-neutron capture in gaseous and liquid trimethylphosphine, has been described, and the extent of failure of bond rupture has been found to be less than 0.1% of the total reaction. The experiments with trimethylphosphine had not enabled definite conclusions to be reached on the contributions of "hot" and thermal reactions to the formation of phosphorus-32-labelled recoil products. "Hot" reactions are recognised in that their yield is independent of temperature or of small concentrations of radical scavengers, but is decreased by addition of moderators such as rare gases which provide for collisional deactivation of high-energy intermediates.⁴ The only indication favouring a thermal mechanism following neutron capture in trimethylphosphine was that the yield of [³²P]-phosphine following irradiation of liquid trimethylphosphine at -78° was one fifth of that after irradiation of the gaseous substance at room temperature. On the other hand, addition of rare gases caused a marked decrease in the yields of volatile products.

During the neutron activation of tri-n-butyl phosphate⁵ and of phosphorus trichloride,⁶ both "hot" and thermal reactions have been recognised.

In the present study, scavenger and moderator effects on the yields of phosphorus-32-labelled products, after neutron activation of gaseous phosphine, have been investigated.

RESULTS

In most experiments, phosphine mixed with an excess of either methane or a rare gas, or with an excess of a mixture of methane and a rare gas, was sealed in quartz tubes and irradiated in the thermal column for 10–30 hr. The results are given in Tables 1 and 2. The major phosphorus-32-containing product was phosphine. "Other volatiles" in Table 1 includes methylphosphines, as well as a small percentage of the phosphine activity, *ca.* 0.6% of the total activity, which tailed out of the gas-chromatography column after the bulk of the phosphine had been collected. (In runs 94, 96, and 97, in which no methane was present and thus no methylphosphine could be formed, this percentage was $0.6 \pm 0.1\%$.) "Percentage recovery," the last column in Tables 1 and 2, refers to the total recovered yield: $100 \text{ ("PH}_3\text{"} + \text{"Other volatiles"} + \text{"Non-volatiles"})/\text{calculated yield}$. The calculated yield is based on the phosphorus-32-activity induced in triphenylphosphine samples irradiated in the vicinity of the gas ampoules.

¹ Part II, Halmann and Kugel, *J. Inorg. Nuclear Chem.*, 1963, **25**, 1343.

² Halman, *Proc. Chem. Soc.*, 1960, 289; "Chemical Effects of Nuclear Transformations," Internat. Atomic Energy Agency, Vienna, 1961, Vol. I, p. 197.

³ Halmann and Kugel, *Bull. Res. Council Israel*, 1961, **10A**, 124; *ibid.*, 1962, **11A**, 205.

⁴ Estrup and Wolfgang, *J. Amer. Chem. Soc.*, 1960, **82**, 2661, 2665; Milmann, *Radiochim. Acta*, 1963, **1**, 15.

⁵ Siuda, *Nukleonika*, 1962, **7**, 624.

⁶ Drawe and Henglein, *Z. Naturforsch.*, 1962, **17b**, 486; Henglein, Drawe, and Perner, *Radiochim. Acta*, 1963, **2**, 19.

TABLE 1.

Search for moderator effects on yields (%) of phosphorus-32-containing products after neutron capture in gaseous phosphine.

Run no.	Irradn. time (hr.)	Target mixture (pressures in mm. Hg)			Distribution of ^{32}P in products			Percentage recovery
		PH_3	CH_4	Rare gas	PH_3	Other volatiles	Non-volatiles	
94	25	29			59	0.7	40.3	97
27	103	5.5	550		48.6	4.1	40.0	
84	17.7	43	505		44.8	0.9	54.6	118
86	17.7	17	450		45.6	2.8	51.6	122
110	35	26.5	380	Xe, 50	46.0	0.5	53.5	103
111	35	26	255	Xe, 175	47.8	0.3	51.9	113
112	35	25	85	Xe, 420	47.8	0.4	51.8	98
113	35	28.5	325	Kr, 92	55.2	0.3	44.5	99

TABLE 2.

Search for scavenger effects on yields (%) of ^{32}P -containing products after neutron capture in gaseous phosphine.

Run no.	Irradn. time (hr.)	Target mixture (pressures in mm. Hg)				Distribution of ^{32}P in products			Percentage recovery
		PH_3	CH_4	Argon	Scavenger †	PH_3	Other volatiles	Non-volatiles	
87	28.8	44	490		H_2O , 1.4	43.5	2.2	54.2	102
28	106	5.7	670		H_2O , 0.8	45.0	11.3	43.5	
97	25	24			O_2 , ca. 1	68.9	0.7	30.4	102
96	25	26		455	O_2 , ca. 1	59.0	0.5	40.5	92
120*	178	29	460		CCl_4 , 6.3	51.0	4.9	44.1	
121*	178	22	470		CCl_4 , 11.7	46.3	0.2	53.5	
122*	178	21	450		CCl_4 , 4.0	46.7	0.8	52.5	
105	189	27	455		C_6H_{10} , 1	51.4	1.9	47.7	120
106	189	24	465		C_6H_{10} , 3	39.3	1.1	59.6	107
104	189	27	465		C_6H_{10} , 7	44.6	1.3	54.1	100
107	189	27	470		C_6H_{10} , 12	57.7	1.3	41	134
108	189	25	480		C_6H_{10} , 28	47.5	0.5	51	133
109	189	28	470		C_6H_{10} , 37	47.3	0.7	53	101
118	35	24.5	135	380	C_6H_{10} , 4	50.1	0.4	49.5	97
119	35	25.5	215	215	C_6H_{10} , 5	39	0.4	60.6	100
79		17.5			NH_3 , 500	69	0.8	30.2	85

* Separation of phosphine from methylphosphines by low-temperature distillation. † C_6H_{10} cyclohexene.

Irradiations in the absence of methane usually resulted in higher retention as [^{32}P]phosphine. The highest retention yield, 69%, was obtained in the presence of 500 mm. of ammonia (Run 79). Apparently, here, the preferred reaction of the recoiling phosphorus-32 atoms was hydrogen abstraction from the ammonia molecules. Similarly, irradiation of phosphine with or without added oxygen or argon (runs 94, 96, and 97) resulted in retention yields, as [^{32}P]phosphine, of $64 \pm 5\%$.

As seen from Tables 1 and 2, the yield of phosphorus-32 in the phosphine fraction, in the presence of methane, was remarkably independent of changes in environmental conditions. Thus, after irradiation of mixtures of phosphine and methane (runs 27, 84, and 86), or of mixtures of phosphine, methane, and small amounts of water (runs 87 and 28), carbon tetrachloride (runs 121 and 122), or cyclohexene (runs 104—109), the yield of phosphorus-32-labelled phosphine was always between the same limits, $50 \pm 10\%$. Similarly, replacing part of the methane by argon, krypton, or xenon also did not cause any significant change in the yield of [^{32}P]phosphine (runs 96, 110—113, and 118 and 119). The smaller retention as [^{32}P]phosphine after irradiations in the presence of methane may be due to the competition of reactions of recoiling phosphorus-32 atoms to form phosphorus-carbon bonds.

Paper-chromatographic separation³ was carried out for the non-volatile products formed after neutron capture in mixtures of phosphine, methane, and carbon tetrachloride (run 122). Of the 52% activity in this non-volatile fraction, 36% was contained

in inorganic P-H compounds (H_3PO_3 and H_3PO_2) and 16% in P-Me compounds [MePO_3H_2 and $\text{Me}(\text{H})\text{PO}_2\text{H}$].

DISCUSSION

The $^{31}\text{P}(n, \gamma)^{32}\text{P}$ reaction results in a cascade of gamma quanta, which are able to impart to the newly formed phosphorus-32 atom a recoil energy which is many times larger than that required to undergo chemical reactions.⁷ Thus, essentially all recoiling phosphorus-32 ions or atoms are initially of very high electronic and kinetic energy, but they are deactivated by collisions and charge transfer with gas molecules to form what are probably neutral ground-state phosphorus atoms (spectroscopic designation, $4 S_{3/2}$)⁸ which are certainly very reactive towards molecules such as phosphine, oxygen, or water, present in the gaseous medium.

Ion-Molecule Reactions.—Such reactions of the recoiling phosphorus species cannot be ruled out in a medium containing a large mole fraction of phosphine, because the ionisation potential of the phosphorus atom (11.0 eV) is higher than that of phosphine (10.3 eV),⁹ and therefore a charge-transfer reaction, *e.g.*,



should be possible. However, the ionisation potential of cyclohexene, 9.2 eV,^{9b} is even lower, but its presence (see Table 2) had no effect on the retention in gaseous phosphine.

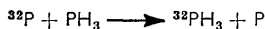
"Hot" Reactions.—In the neutron activation of phosphine, the recoiling "hot" phosphorus-32 atom (or ion) could either have abstracted hydrogen atoms from phosphine molecules, abstracted hydrogen or carbon atoms from methane, or been moderated by more-or-less elastic collisions with methane or rare-gas molecules. The observed lack of effect of rare gases on the yield of [^{32}P]phosphine indicates that its formation is essentially *not* due to a "hot" (high kinetic energy) reaction.

An alternative explanation of the lack of effect of inert gases is that both "hot" and thermal reactions give the same products.

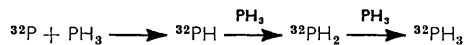
Thermal Reactions.—The alternative mechanism, formation of phosphine by a thermal reaction, may in principle be tested by studying the effect of radical scavengers, which even in small amounts should be able to trap a thermal reaction intermediate. Unfortunately, no suitable scavengers for reactions of thermal phosphorus atoms have been reported. None of the compounds tried, water, oxygen, carbon tetrachloride, or cyclohexene, had any marked effect in our system. The simplest explanation that we can offer is that phosphine molecules themselves were so much more effective than the above compounds tested as scavengers, that the effect of the latter was negligible.

Both oxygen and iodine had a pronounced influence on the distribution of products following neutron capture in liquid tri-*n*-butyl phosphate.⁵ It is, however, possible that this effect is due to scavenging of alkyl radicals formed in the cage surrounding the recoiling phosphorus-32 atom. Cyclohexene has been used as a scavenger for thermal reactions in the neutron activation of phosphorus trichloride, but this effect has been recognised as being due to trapping of chlorine atoms.⁶

It is still unknown whether the final stabilisation of the phosphorus-32 atom occurs by a one-stage reaction, such as



or if several intermediate stages are involved, *e.g.*,



⁷ Bartholomew and Higgs, "Compilation of Thermal Neutron Capture Gamma Rays," AECL No. 669, Atomic Energy of Canada Ltd., 1958, p. 25; Cifka, *Radiochim. Acta*, 1963, **1**, 127.

⁸ Moore, "Atomic Energy Levels," Nat. Bureau Standards, Circular No. 467, Washington D.C., 1949, Vol. I, p. 163.

⁹ (a) Fischler and Halmann, *J.*, 1964, 31. (b) Field and Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press, New York, 1957.

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This problem could possibly be solved by a double-labelling technique. After neutron irradiation of a mixture of PH_3 and PD_3 , the one-stage mechanism should produce $^{32}\text{PH}_3$ and $^{32}\text{PD}_3$, but no $^{32}\text{PH}_2\text{D}$ or $^{32}\text{PHD}_2$.

Obviously, the non-occurrence of a "hot" reaction in gaseous phosphine does not mean that reactions of "hot" phosphorus atoms are not possible in other systems.^{5,6} The difference between the results for phosphorus recoil in liquid and gaseous systems may be similar to that observed in liquid and gaseous methyl iodide.¹⁰ Recoiling iodine atoms, following neutron capture in the gas phase, do not seem to form stable products until they have reached thermal energies.

EXPERIMENTAL

The preparation of phosphine and the neutron-irradiation conditions have been described.¹⁻³ All irradiations were carried out in the thermal column of the Israel Research Reactor No. 1 at a thermal-neutron flux of 2×10^{10} neutron cm^{-2} sec^{-1} . Separation of phosphorus-32-labelled products was carried out either by gas chromatography or by low-temperature distillation in a vacuum system in which the phosphine fraction was isolated by distillation from -78 to -196° , and the "Other volatiles" fraction from 25 to -196° . The "Non-volatile" fraction was rinsed off the quartz ampoules with nitric acid. All fractions were oxidised with nitric acid. Portions were evaporated on aluminium plates and counted under end-window proportional counters.

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¹⁰ Lawrence and Stranks, "Radioisotopes in Physical Sciences and Industry," Internat. Atomic Energy Agency, Vienna, 1962, Vol. III, p. 483.
