J. Inorg. Nucl. Chem., 1957, Vol. 5, pp. 31 to 47. Pergamon Press Ltd., London

NEUTRON IRRADIATION OF SOME CRYSTALLINE SALTS OF PHOSPHORIC, PHOSPHOROUS, AND HYPOPHOSPHOROUS ACIDS IN VACUUM*

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(*Received* 6 *March* 1957)

Abstract—The radioactive products obtained by the neutron plus gamma irradiation of phosphorus compounds depend upon the conditions of the irradiation and upon the nature of the compounds irradiated. In vacuum, where easily oxidized, neutron activation products such as elemental phosphorus or phosphine should be recoverable, the principal radioactive irradiation product of anhydrous Na_2HPO_4 was phosphate, which was accompanied by traces of phosphorus and several unidentified products. The principal radioactive irradiation products of anhydrous Na_2HPO_3 and NaH_2PO_2 were phosphite and hypophosphite accompanied by a little phosphate and phosphorus. Neither phosphine nor diphosphine was detected as an irradiation product of these salts. The principal neutron irradiation products of PH_3 were H_2 and radioactive PH_3 and P. As shown by analysis, most of the radioactive products were formed in chemically detectable quantities, but the specific activity of these products was greater than that of the irradiated substances themselves.

In vacuum, gamma rays alone scarcely altered Na_2HPO_4, but they converted Na_2HPO_3, NaH_2PO_2 and PH_3 into the same products formed by neutrons plus gamma rays.

In the reactor where the gamma rays accompanying the neutrons are very intense, the final neutron irradiation products of Na_2HPO_4, Na_2HPO_3, and NaH_2PO_2 in vacuum were the primary neutron activation products, the gamma-ray alteration products of these primary activation products, and the neutron activation products of the gamma-ray modifications of the original salts.

Slight alteration of the phosphate by neutrons plus gamma rays indicates that the dissipation of the nuclear energy after the absorption of a neutron does not disrupt the chemical bonds of the recoiling atoms in nearly all instances. The formation of similar products by gamma irradiation and by neutron plus gamma irradiation of phosphite and hypophosphite indicates that the gamma-induced reactions and the neutron-induced reactions have similar but not necessarily identical mechanisms.

When pure crystalline compounds are irradiated with neutrons, some of the atoms that absorb the neutrons remain in their original chemical form even though the energy of the accompanying nuclear rearrangements is sufficient to rupture all their chemical bonds. Other similar atoms that absorb the neutrons are converted into a variety of chemical species depending upon the element, upon the compound irradiated, and upon the experimental conditions.(1-3)

In the case of crystalline, hydrated phosphates, ($NaH_2PO_4 \cdot H_2O$, $Na_2HPO_4 \cdot 12H_2O$, and $Na_3PO_4 \cdot 12H_2O$), bombarded in air with neutrons from a Ra-Be source, Libby(1) reported that some 30 to 50 per cent of the radioactive phosphorus atoms remained as phosphate. This conclusion was based upon the observation that about 30 to 50 per cent of the radioactive phosphorus was precipitated from solutions of the irradiated

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* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

(1) W. F. Libby *J. Amer. chem. Soc.* **62**, 1930 (1940).

(2) A. G. Maddock *Research* **2**, 556 (1949).

(3) J. G. A. Fiskell, W. A. DeLong, and W. F. Oliver *Canad. J. Chem.* **30**, 9 (1952).

salts as magnesium ammonium phosphate. The chemical form of the unprecipitated phosphorus was not reported. With $Na_2HPO_3 \cdot 5H_2O$ irradiated in air, some 92 per cent of the radioactive phosphorus remained in a form oxidizable to phosphate with bromine, and this was presumed to be phosphite. With similar methods of analysis, Aten(4) found that irradiation of $Na_2SO_4 \cdot 10H_2O$ produced radioactive phosphorus compounds with 91 per cent as phosphate and 9 per cent as an unidentified reduced form, presumably phosphite. Likewise, irradiation of $Na_2SO_3 \cdot 7H_2O$ produced radioactive phosphorus compounds with 40 per cent as phosphate and 60 per cent oxidizable to phosphate and presumed to be phosphite. Thomas and Nicholas(5) found that irradiation of Na_2HPO_4 under unspecified conditions in the Harwell reactor yielded only 50 per cent of the activity as phosphate and the remainder in chemical species convertible to phosphate by treatment with concentrated nitric acid and 60 per cent perchloric acid.

After irradiation of dried monocalcium phosphate at the Chalk River Laboratories, Fiskell, Delong, and Oliver(3) reported 30 per cent of the phosphorus activity as phosphate, determined as the molybdate, 45 per cent as hypophosphate, determined as silver salt or as the bromine oxidation product precipitable with molybdate, and about 16 per cent (the difference between the silver-salt activity and the zinc-salt activity) attributed to pyrophosphate. Tricalcium phosphate yielded 38 per cent phosphate, 36 per cent hypophosphate, and 32 per cent metaphosphate, determined as the barium salt after demineralization in an Amberlite IR-100 column. Fiskell, Delong, and Oliver(3) did not find phosphine among the irradiation products of phosphates. They did, however, report a radioactive gas, presumably phosphine, among the irradiation products of calcium hypophosphite.

Aten, Van Der Straaten, and Riesebos(6) irradiated several crystalline phosphates with neutrons from the cyclotron (without specification of the irradiation conditions). They then separated the pyrophosphate, with carrier, as the zinc and cadmium salts which were hydrolysed to phosphate and estimated as magnesium ammonium phosphate, leaving a small amount of activity attributed to phosphite and hypophosphite. Phosphate was determined, with carrier, as the magnesium ammonium phosphate, leaving much residual activity attributed to phosphite plus hypophosphite. From the average of the results and with the two fractions of phosphite plus hypophosphite added together, the proportional distribution of the activity from the several irradiated compounds was:

Na_2HPO_4	PO_4,	0·23	P_2O_7, 0·25	$PO_3 + PO_2$, 0·53
$Na_2HPO_4 \cdot 2H_2O$	PO_4,	0·22	P_2O_7, 0·18	$PO_3 + PO_2$, 0·59
$Na_2HPO_4 \cdot 5H_2O$	PO_4,	0·12	P_2O_7, 0·07	$PO_3 + PO_2$, 0·82

A more comprehensive analysis of the neutron irradiation products of phosphate has been obtained by differential electrical migration in lactic acid solution stabilized with soft filter paper. With this electrochromatographic method of separation, the mixture of the radioactive, neutron irradiation products formed in air has been resolved without loss of any of the components. For example, Norris, Sato, and

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(4) A. H. W. Aten, Jr. *Rec. trav. chim.* **61**, 467 (1942).

(5) W. D. E. Thomas and D. J. D. Nicholas *Nature, Lond.* **163**, 719 (1949).

(6) A. H. W. Aten, Jr., H. Van Der Straaten, and P. C. Riesebos *Science* **115**, 267 (1952).

STRAIN[7] observed that neutron irradiation of phosphates, including NaH_2PO_4, $CaHPO_4$, apatite and bone, followed by electrochromatographic analysis, yielded primarily radioactive phosphate plus several unidentified species of phosphorus compounds. The nature and the proportions of these products separated by electrical migration varied with the chemical form and the previous treatment of the phosphate that was irradiated. Electrochromatographic comparison of these neutron activation products with authentic phosphorus compounds by SATO, NORRIS, and STRAIN[8] indicated that the principal product was usually the substance that was irradiated. Hypophosphorus acid, which occurs among the minor radioactive products, migrated faster than phosphate. In illustrating the importance of differential migration methods of analysis to agriculture, STRAIN and SATO[9] showed that phosphite is also a neutron activation product of certain phosphorus compounds. The phosphite formed a migrating zone between the phosphate and the hypophosphite. Pyrophosphate, formed from some phosphorus compounds, migrated along with the hypophosphite, but with a little zinc salt in the lactic acid, the pyrophosphate precipitated at the starting point while the other acids of phosphorus migrated through the medium.

Utilization of the electrochromatographic method of analysis also revealed that complex condensed phosphates probably occur among the neutron-irradiated phosphorus compounds. SATO, KISIELESKI, NORRIS, and STRAIN[10] found that certain condensed phosphates migrate slower than phosphate. SATO and NORRIS[11] and SATO, NORRIS, KISIELESKI, SMETANA, and STRAIN[12] demonstrated that condensed phosphates similar to slowly migrating products formed in neutron-irradiated phosphate[7] arise from heating phosphate and from the gamma-ray irradiation of phosphate.

Most of the neutron irradiations of phosphate were carried out in air in nuclear reactors where the samples were exposed to a high intensity of gamma rays as well as to neutrons. Easily oxidizable irradiation products, such as phosphorus, phosphine, or diphosphine, might, therefore, have been converted into various oxidation products. Moreover, the gamma rays might produce chemical changes, such as condensation, before reaction of the phosphates with neutrons. They might also produce chemical changes of the primary neutron irradiation products. In addition to the primary neutron activation products, the final neutron irradiation products of phosphates might therefore contain oxidized primary neutron irradiation products, gamma irradiation products of the various oxidation products of the phosphates themselves, and neutron activation products of these gamma irradiation products.

In order to collect further information about the neutron activation products of phosphate and to gain a better insight into the mechanism of neutron reactions with chemical compounds, we have now irradiated anhydrous phosphate (Na_2HPO_4), phosphite (Na_2HPO_3), and hypophosphite (NaH_2PO_2) with gamma rays and with

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(7) W. P. NORRIS, T. R. SATO, and H. H. STRAIN *Quarterly Report, Division of Biological and Medical Research* p. 69. Argonne National Laboratory, ANL-4745 (1951–1952).

(8) T. R. SATO, W. P. NORRIS, and H. H. STRAIN *Abstracts of papers* p. 43. 124th meeting Amer. Chem. Soc. Chicago (1953).

(9) H. H. STRAIN and T. R. SATO *A Conference on the Use of Isotopes in Agriculture* pp. 175–182. (Held January 1956). U.S. Atomic Energy Commission, TID-7512, Washington, D.C.

(10) T. R. SATO, W. E. KISIELESKI, W. P. NORRIS, and H. H. STRAIN *Anal. Chem.* **25**, 438 (1953).

(11) T. R. SATO and W. P. NORRIS *Quarterly Report, Division of Biological and Medical Research* p. 62. Argonne National Laboratory, ANL-5247 (1954).

(12) T. R. SATO, W. P. NORRIS, W. E. KISIELESKI, F. SMETANA, and H. H. STRAIN *Quarterly Report, Division of Biological and Medical Research* p. 83. Argonne National Laboratory, ANL-5576 (1956).

neutrons plus gamma rays. To prevent oxidation of the products, we have performed the irradiations in vacuum. We have removed the gaseous products and have analysed them with the mass spectrometer. We have separated the non-volatile products by electrochromatography, and we have compared these products with authentic preparations of various phosphorus compounds. We have also studied the effect of neutrons plus gamma rays and the effect of intense gamma rays alone upon phosphorus, upon phosphorus plus hydrogen, and upon phosphine. With all these phosphorus compounds, we have determined the chemical yields of the irradiation products as well as the radiochemical yields of the radioactive products.

EXPERIMENTAL

Materials for irradiation

Most of the salts for the irradiations were anhydrous, commercial preparations of disodium phosphate, disodium phosphite, and monosodium hypophosphite. The disodium phosphate was also prepared from phosphoric acid and sodium hydroxide. In preparation for the irradiations, 0·01 formula weight of each salt was placed in quartz tubes (2 × 5 cm) provided with a narrow neck (about 2 mm × 7 cm). These tubes were evacuated to a few microns pressure overnight, thus removing most sorbed water and all but minute traces of air. The tubes were then sealed, leaving a narrow neck several centimetres long, and a file mark was made about a centimetre from the sealed tip.

Phosphine was prepared by careful decomposition of phosphonium iodide with water. For this purpose, phosphorus-diphosphorus tetraiodide was prepared from phosphorus and iodine.(13) This tetraiodide was hydrolysed to phosphonium iodide and phosphoric acid, the former being isolated by sublimation. Phosphine was generated in vacuum by the careful addition of water to the phosphonium iodide. The gas was condensed with a bath of liquid nitrogen; any hydrogen was removed with the vacuum pump; and the phosphine was allowed to vaporize at the temperature of a carbon dioxide bath. A portion of this vaporized, dry phosphine (about 13 ml) was measured in a burette and transferred to an evacuated quartz tube of about 30 ml capacity. The connection to the tube was closed, and the phosphine was condensed with liquid nitrogen, while the quartz tube was sealed, a precaution that prevented decomposition of the phosphine by heat.

Red and yellow phosphorus were commercial preparations. Hydrogen, tested for purity with the mass spectroscope, was taken from a cylinder.

Irradiation

The salts and the phosphine were exposed to neutrons plus gamma rays in the vertical thimbles of the Argonne Reactor (CP-5), where the neutron flux was about 10^{13} neutrons per square cm per sec, where the gamma-ray radiation was roughly 500,000 r per min, and where the temperature was about 40 to 50°C. The energy from the absorbed gamma rays was, therefore, many times greater than the energy produced by recoil of the activated phosphorus atoms. Most exposures were for 48 hours. The irradiation turned the quartz tubes containing the salts a deep purple-blue, but it turned the tubes containing the phosphine red-blue, due apparently to a red deposit on the inside.

(13) J. B. WORK *Inorganic Syntheses* (Edited by W. C. FERNELIUS) Vol. II. p. 141. McGraw-Hill, New York (1946).

The salts and the phosphine were exposed to gamma rays alone in the Argonne High-level Gamma-irradiation Facility, where the gamma rays are obtained from spent reactor-fuel elements. Exposures were made for 2 days and for 7 days, providing total gamma irradiation of 1 or 3×10^8 r. In 7 days, the gamma irradiation was only about one-fifth that received by samples placed in the reactor for 2 days ($1{\cdot}5 \times 10^9$ r). This gamma irradiation turned the quartz tubes containing the salts purple-blue, but those containing the phosphine a light brown-blue, due also to a thin red deposit on the inside.

Analysis

Gases. For analysis of the gases liberated by irradiation, the tubes containing the irradiated phosphorus compounds were placed in a larger tube, which was joined to a vacuum apparatus with a large standard-taper joint. This joint was sealed to a short tube about 1 cm in diameter, and this tube was sealed, in turn, at right angles, to the base of a vacuum-type stopcock. The hollow plug of the stopcock was provided with a sturdy eccentric glass projection extending into the base, and the exit tube was bent at right angles and sealed to a small tapered joint connecting horizontally with the vacuum line. By tilting the large tube and stopcock about the axis of this connection, the constricted, sealed tip of the tube containing the irradiated substances could be brought into the base of the stopcock. After the system was evacuated, a turn of the stopcock broke the constricted, sealed tip of the quartz tube and released the gases. These gases were transferred to a burette, measured, and then transferred to an evacuated glass tube provided with a stopcock and standard taper joint. They were analysed with the mass spectrometer, which provided very precise values for the molecular ratios. A special search was made for gases or vapours that might have been formed, as for example, hydrogen and diphosphine (P_2H_4, mol. wt. 66).(14) Analysis of pure phosphine revealed traces of hydrogen and of masses 33 and 32, the two latter corresponding to phosphine less one and two atoms of hydrogen, formed presumably by the dehydrogenation of phosphine itself in the mass spectroscope.

Electrochromatography. For separation of the non-volatile irradiation products, the irradiated salts were transferred to volumetric flasks (100 ml) and dissolved in water forming 0·1 formula weight solutions. The various oxyacids and any suspended free phosphorus contained in these solutions were separated by electrochromatography in a soft, acid-washed, commercial filter paper moistened with dilute acids. One migration procedure employing 0·1 M lactic acid was designed to facilitate semi-quantitative estimation of the irradiation products with a Geiger-Müller counter. A slightly different procedure employing acetic and phosphoric acids as well as lactic acid as the background electrolytic solutions was utilized to confirm the identity of the irradiation products located by radioautography of the electrochromatograms.

As noted already, zinc ions in the background electrolytic solution precipitate pyrophosphate near the starting point, while other oxyacids of phosphorus migrate through the medium.(9) A similar effect has been observed by the use of unwashed filter paper which contains magnesium and calcium salts. If this precipitation effect is to be avoided, special care must be exercised in washing and handling the filter paper.

For acid-leaching of the paper, Eaton-Dikeman filter paper (Grade 301, 0·03 inch

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(14) E. C. Evers and E. H. Street, Jr. *J. Amer. chem. Soc.* **78**, 5726 (1956).

thick) in sheets about 2 ft wide and 6 ft long or in strips 3 in. wide and 6 ft long was encased in a polyethylene sheet and washed with M nitric acid by siphonage and downward percolation for 24 hours. The paper was then washed with distilled water for 3 or 4 days and dried in air on a table covered with clean polyethylene sheeting.

For regulation of temperature during the migrations, sheets or parallel strips of moistened paper were supported on a specially constructed, electrically insulated, flat, level, stainless-steel vessel through which water at nearly constant temperature could be circulated. For the construction of this combined support and temperature regulator, a stainless-steel pan 1 cm deep, 2 ft wide, and 5 ft long, was reinforced internally with parallel longitudinal stainless-steel I-bars 1 cm high. These I-bars extended to within 10 cm of each end of the pan and were spot-welded to the bottom at 10-cm intervals. The pan was covered with a stainless-steel sheet that was welded to the edge of the pan and spot-welded to the reinforcing bars at 10-cm intervals. An outlet and inlet tube were welded at one side near the ends. This flat vessel or tank was insulated electrically with a wrapping of two layers of polyethylene sheeting each 0·005 in. thick.

For the differential electrical migrations, a strip of polyethylene sheeting 2 ft wide was placed on the insulated, water-cooled tank, and a wide sheet or parallel strips of the acid-washed paper were placed on the polyethylene. The paper was moistened with 0·1 M lactic acid solution, and the excess solution was allowed to drain into large plastic electrode vessels at the ends of the tank. These electrode vessels were prepared from blocks of polymerized solidified polystyrene foam 2 ft 6 in. long and 6 in. square that were hollowed out by narrow parallel cuts with a circular saw to produce a cavity 2 ft 3 in. long, 3 in. wide, and 3 in. deep. The moistened paper was blotted lightly with clean paper towels, and each end was dipped into about 3 litres of the lactic acid solution in each electrode vessel. The moist paper between the solutions in the electrode vessels (162 cm long) was covered with a sheet of polyethylene, and a siphon was used to level the liquid in the two vessels. This system was allowed to stand for about 6 hours. The polyethylene cover was removed momentarily, and the solutions (100 μl) of the mixtures were placed at separate marked points in a line about 10 cm from the end of the stainless-steel tank near the cathode. In the paper sheets, these starting spots were about 3 in. apart. In the narrow paper strips, one spot was placed on each strip. The paper was then covered again with the polyethylene, and d.c. electrical potential (about 800 V or 5 V per cm) was applied to the large graphite electrodes (nuclear reactor graphite, grade CS) for 24 to 30 hours (current, about 30 mA). After this electrolysis, the ends of the paper in the electrode vessels were cut off, the upper polyethylene sheet was removed, and the paper was allowed to dry in air. For purposes of identification, authentic preparations of the various phosphorus compounds were allowed to migrate alongside the irradiated samples.

The phosphorus compounds were also separated by electrical migration in 0·1 M acetic acid and in 0·05 M phosphoric acid, which were stabilized in wide sheets of acid-washed paper. These separations were made with the apparatus previously described.(10)

Detection of radioactive zones. For the location of radioactive phosphorus compounds separated by electrical migration and for their semiquantitative estimation, the paper was scanned with a shielded proportional Geiger-Müller counter fitted with a Mylar window 1 in. wide and 3 in. long and supplied with a 10 per cent mixture of methane in argon. This counter, with a background of about 80 counts per min, was mounted horizontally on a brass plate $\frac{1}{2}$ in. thick, with an opening or window 1 in. wide and 3 in. long. This brass plate, with the counter tube attached above it, was mounted $\frac{1}{8}$ in. above two square brass bars which were parallel to the opening in the counter. These two brass bars were 1 in. thick, 1 in. apart, and $\frac{3}{8}$ in. above the paper to be scanned.

Wide paper to be scanned was cut into strips 3 in. wide and 3 ft long. These sections and the similar narrow strips employed for separate migrations were fastened to an aluminium strip, 3 in. wide and 3 ft long, with masking tape. The metal strip with the attached paper was then pulled under the counter, about 1·5 cm at a time, and the radioactivity was determined.

For the detection and location of the radioactive products separated by migration in 0·1 M acetic acid and in 0·05 M phosphoric acid, radioautographs were made with Kodak "No-screen" X-ray film. The separated substances were identified by reference to authentic preparations submitted to migration in the same sheet of filter paper.

Detection of non-radioactive zones. Non-radioactive phosphorus compounds separated by electrical migration in moist paper were located by neutron activation. For this activation, the paper was dried, placed on a sheet of polyethylene, and the two sheets were rolled together, providing a roll about 3 in. in diameter. This rolled paper was wrapped in aluminium foil and placed in the thermal column of the reactor for about a week at a neutron flux of approximately 10^{12} neutrons per sec. When removed from the reactor, the paper was permitted to "cool" for some 7 to 14 days to reduce the background of the paper itself. It was then unrolled, kept straight under iron rods for a day or two, and finally taped to the metal strips for measurement of the activity with the Geiger counter. Owing to the brittleness of the irradiated paper and to the unevenness of the paper strips under the counter, the background counts were not as uniform as those of paper in which radioactive substances had been separated.

Chemical analysis. For estimation of the chemical yields of the irradiation products, the principal components of the irradiated phosphorus compounds were determined by chemical methods. Phosphate was estimated photometrically as the phosphovanadomolybdate.(15) Phosphite was determined by oxidation with iodine in neutral solution.(16) Hypophosphite was ascertained by oxidation with ceric ions in acid solution.(17) Pyrophosphate was estimated by precipitation with tris(ethylenediamine)-cobalt(III) chloride at pH 7.(18) Phosphorus was not determined and may have interfered with the analysis for other substances.

RESULTS

Separation of mixtures. For the electrochromatographic comparisons and for chemical analysis, freshly prepared solutions of the salts were employed. To show that some common acids of phosphorus migrate at different rates, solutions of the inactive, non-irradiated salts were submitted to migration in separate strips of paper placed side by side on the support with their ends dipping into the same electrode vessels. The location of the zones, after migration, activation, and scanning, is shown in Fig. 1.

(15) C. J. Barton *Anal. Chem.* **20**, 1068 (1948).

(16) R. T. Jones and E. H. Swift *Anal. Chem.* **25**, 1272 (1953).

(17) D. N. Bernhart *Anal. Chem.* **26**, 1798 (1954).

(18) H. W. McCune and G. J. Arguette *Anal. Chem.* **27**, 401 (1955).

The separation of oxyacids of phosphorus from their mixtures by electromigration is shown by Fig. 2. Here the non-irradiated salts were mixed before migration. With a mixture containing pyrophosphate in addition to the three other acids, the hypophosphite and the pyrophosphate formed a single zone well separated from the phosphate and the phosphite. Similar results were also obtained with hypophosphate, which formed a zone migrating at nearly the same speed as pyrophosphate and hypophosphite.

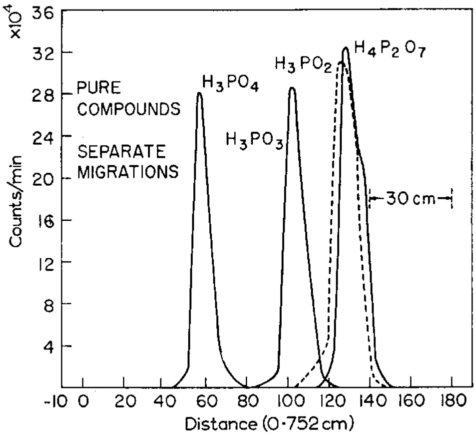

Fig. 1.—Zones of H_3PO_4, H_3PO_3, H_3PO_2, and $H_4P_2O_7$ after simultaneous migration in *separate*, parallel strips of filter paper. Located after activation with neutrons. Background solution, 0·1 M lactic acid. Time, 24 hours. D.C. potential, about 5 V per cm.

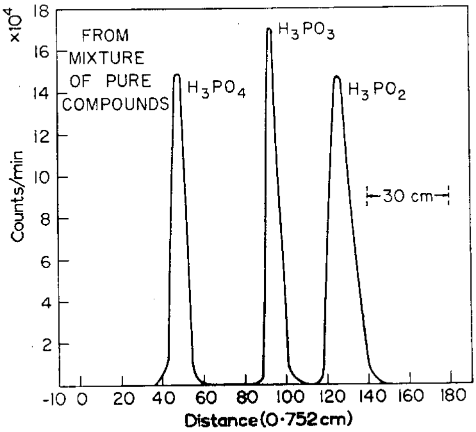

Fig. 2.—Zones of H_3PO_4, H_3PO_3, and H_3PO_2 separated by migration from a single spot in a strip of paper. Located after activation with neutrons. Background solution, 0·1 M lactic acid. Time, 24 hours. D.C. potential, about 5 V per cm.

Neutron-irradiated Na_2HPO_4. When the evacuated tubes containing neutron-irradiated Na_2HPO_4 were opened, only a trace of gas was observed, and this proved to be hydrogen (Table 1). Phosphine and diphosphine were not detected. When the irradiated salt was dissolved in water, a faint phosphorus-like odour was observed, and the solution had a barely perceptible yellow colour. Exposed to air, the solution became colourless after several days, but, treated with bromine water or hypochlorite, the solution was decolorized almost instantly.

TABLE 1.—IRRADIATION PRODUCTS OF PHOSPHORUS COMPOUNDS
(Determinations independent of radioactivity)

Compounds	Irradiation	Products (mole per cent)					
		H_3PO_4	H_3PO_3	H_3PO_2	$H_4P_2O_7$	PH_3	H_2
Na_2HPO_4	n,(10^{13} n/s; $2d$)	100	Not detected	Not detected	Not detected	Not detected	Trace
Na_2HPO_3	n,(10^{13} n/s; $2d$)	2·5	89·0	4·0	Not detected	Not detected	$1{\cdot}4\quad 10^{-4}$
NaH_2PO_2	n,(10^{13} n/s; $2d$)	2·0	20·0	62·0	Not detected	Not detected	$3{\cdot}8\quad 10^{-3}$
PH_3	n,(10^{13} n/s; $2d$)	—	—	—	—	56·4	43·6
Na_2HPO_4	γ, (3×10^8 r)	100	Not detected	Not detected	Not detected	Not detected	Trace
Na_2HPO_3	γ_2. (3×10^8 r)	2·0	92·0	4·0	Not detected	Not detected	$1{\cdot}6\quad 10^{-4}$
NaH_2PO_2	γ_2. (3×10^8 r)	0·4	9·0	80·0	Not detected	Not detected	$1{\cdot}1\quad 10^{-3}$
PH_3	γ_2, (3×10^8 r)	—	—	—	—	94·9	5·1

A typical electrochromatogram of Na_2HPO_4 after exposure in the reactor for 2 days is reproduced as Fig. 3. Made in parallel and simultaneously with the migrations represented by Fig. 1, this separation provided a principal zone that must be attributed to phosphate. The proportions of small zones migrating slightly faster and slightly slower than the phosphate zone varied significantly in different irradiation experiments. The zone remaining at the starting point was not found in solutions of the irradiated salt that had been allowed to stand in air for many days or that had been treated with bromine water.

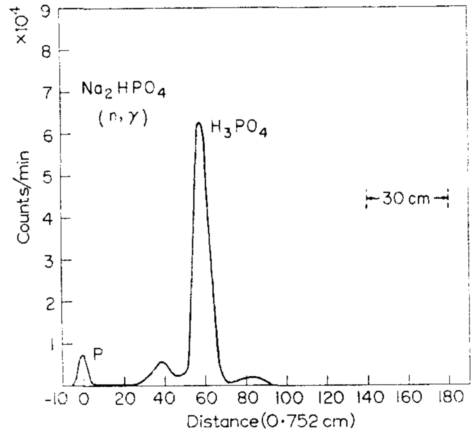

FIG. 3.—Radioactive products formed by neutron plus gamma irradiation of Na_2HPO_4 in vacuum and separated by electrical migration in a strip of paper as in Fig. 2. Zones identified by simultaneous migration of authentic phosphorus compounds which were located by neutron activation, as in Fig. 1.

Chemical analysis (Table 1) did not reveal a decrease in the phosphate content of the neutron-irradiated salt. Neither did it reveal new substances produced from the phosphate.

Gamma-irradiated Na_2HPO_4. The Na_2HPO_4 exposed to gamma rays for 7 days provided only traces of gas, which proved to be hydrogen (Table 1). The solution of the gamma-irradiated salt was faintly yellow, and it was bleached with dilute bromine water. Separated by electrical migration in a strip of paper and then activated with neutrons, the gamma irradiation products yielded the curve shown in Fig. 4. By comparison with the location of phosphate ions in the same sheet of paper, the principal zone was unaltered phosphate. Traces of phosphorus or a phosphorus-like substance remained at the starting point. Chemical analysis did not reveal a detectable change in the phosphate (Table 1).

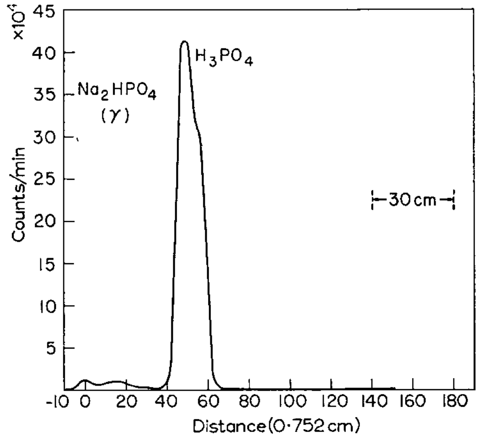

FIG. 4.—Products formed by gamma irradiation of Na_2HPO_4 in vacuum, separated by electrical migration in a strip of paper, and located after activation with neutrons, as in Fig. 1.

Neutron-irradiated Na_2HPO_3. The irradiated Na_2HPO_3 yielded a very small quantity of hydrogen, but no phosphine (Table 1). The salt had a phosphorus-like odour when dissolved in water, and it produced a pale yellow solution. This pale yellow solution was decolorized instantly with bromine water or with sodium hypochlorite. It was also decolorized slowly upon standing in air.

A typical electrochromatogram runs parallel and simultaneously with those shown in Figs. 1 and 3 is reproduced as Fig. 5. By comparison with Fig. 1 the principal zones in the order of their abundance were phosphite, hypophosphite, phosphate, phosphorus, an unidentified substance migrating faster than hypophosphite, and traces of two substances migrating slower and faster than phosphate. The zone at the starting point was not detectable in solutions that had been treated with bromine water.

Separate irradiations of Na_2HPO_3 in vacuum followed by electromigration in acetic acid solution revealed much activity migrating between the phosphate and the phosphite. By contrast, migration in 0·05 M phosphoric acid revealed little or no radioactive material in this region.

Chemical analysis revealed significant chemical changes of the irradiated Na_2HPO_3 (Table 1). Some 11 per cent of the phosphite had disappeared. More than half of this loss was accounted for as hypophosphite and as phosphate. Chemical tests failed to reveal any pyrophosphate (Table 1).

The quartz tube in which the Na_2HPO_3 was irradiated was coated with a very thin layer of a yellow-red, radioactive deposit. This material was insoluble in water, acid, bases, and carbon disulphide. It dissolved rapidly in bromine water. Electrical migration of this oxidized solution in paper moistened with lactic acid yielded two zones corresponding to phosphite and phosphate.

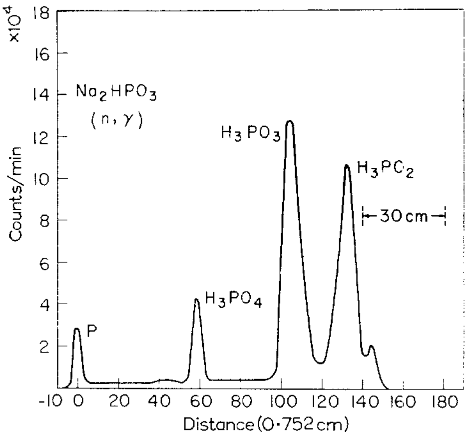

FIG. 5.—Radioactive products formed by neutron plus gamma irradiation of Na_2HPO_3 in vacuum and separated by electrical migration in a strip of paper, as in Fig. 2. Zones identified by simultaneous migration of authentic phosphorus compounds which were located by neutron activation, as in Fig. 1.

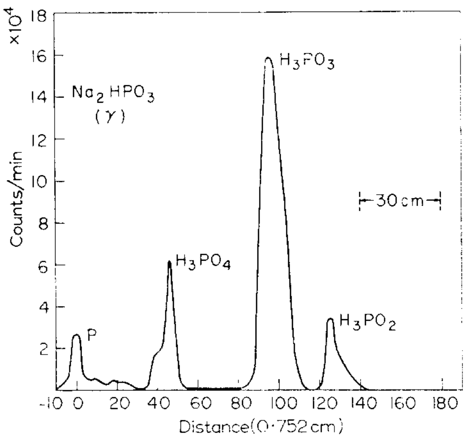

FIG. 6.—Products formed by gamma irradiation of Na_2HPO_3 in vacuum, separated by electrical migration in a strip of paper, and located after activation with neutrons, as in Fig. 1.

Gamma-irradiated Na_2HPO_3. The Na_2HPO_3 exposed to gamma rays for 7 days yielded a very small quantity of hydrogen. This irradiated salt formed a pale yellow solution that was bleached by bromine water.

An electrochromatogram formed in a strip of paper and activated with neutrons is shown in Fig. 6. From this curve, the most abundant products were phosphite, phosphate, hypophosphite, and phosphorus.

Chemical analysis (Table 1) indicated that about 8 per cent of the phosphite had undergone chemical alteration. About 6 per cent was accounted for as hypophosphite and phosphate, the greatest proportion of the alteration products being hypophosphite, whereas the electrical migration indicated that phosphate was as abundant as hypophosphite.

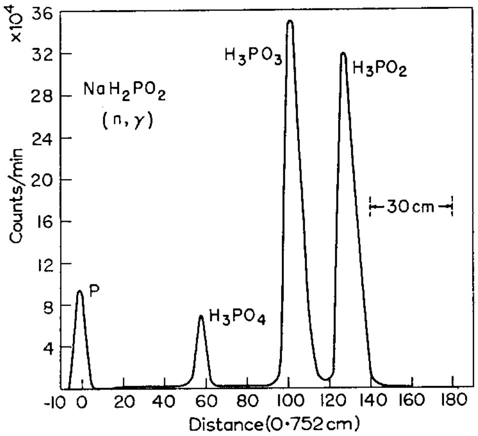

FIG. 7.—Radioactive products formed by neutron plus gamma irradiation of NaH_2PO_2 in vacuum and separated by electrical migration in a strip of paper, as in Fig. 2. Zones identified by simultaneous migration of authentic phosphorus compounds which were located by neutron activation, as in Fig. 1.

Neutron-irradiated NaH_2PO_2. This neutron-irradiated salt yielded a little hydrogen, but no phosphine or diphosphine (Table 1). Solutions were straw-coloured and were decolorized rapidly with bromine water or hypochlorite. They were decolorized slowly upon exposure to air.

An electrochromatogram prepared simultaneously with that shown in Fig. 1 is reproduced as Fig. 7. The principal radioactive irradiation products were phosphite, hypophosphite, phosphorus, and phosphate. The amount of activity in the hypophosphite zone was slightly less than that in the phosphite zone.

Chemical analysis (Table 1) showed that about 38 per cent of the hypophosphite had been altered by the neutron irradiation. About half of this was accounted for as phosphite, and a little more was present as phosphate. Pyrophosphate was not detected. Some 14 per cent of the total phosphorus, including the elemental phosphorus, was unaccounted for.

The quartz tube in which the NaH_2PO_2 was irradiated was coated with a thin, radioactive orange-red deposit. Washed with water, dissolved in bromine water, and submitted to electrical migration, this deposit yielded zones of phosphate and phosphite.

Gamma-irradiated NaH_2PO_2. The hypophosphite, after exposure to gamma rays for 7 days, resembled the neutron-irradiated product. It was sintered together and was light yellow in colour. It provided a trace of hydrogen, and it yielded a straw-coloured solution with a phosphorus-like odour. The solution was bleached rapidly with bromine and slowly upon exposure to air.

An electrochromatogram, prepared in 0·1 M lactic acid and activated with neutrons, provided the activity curve shown in Fig. 8. The most abundant substance was hypophosphite. Phosphite, phosphate, and phosphorus were present in significant quantities relative to that of the phosphite.

Chemical analysis showed that about 20 per cent of the hypophosphite had been altered by the gamma irradiation. Nearly half of this altered hypophosphite was present as phosphite, with a little as phosphate (Table 1). About 10 per cent of the total phosphorus, including the elemental phosphorus, was unaccounted for by the chemical analysis.

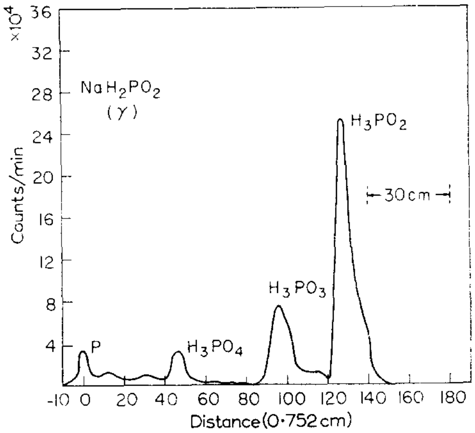

FIG. 8.—Products formed by gamma irradiation of NaH_2PO_2 in vacuum, separated by electrical migration in a strip of paper, and located after activation with neutrons, as in Fig. 1.

As with the neutron irradiation, the walls of the quartz tube had a very thin coating of material insoluble in water but readily soluble in bromine water.

Neutron-irradiated PH_3. Irradiation of the phosphine, at about half an atmosphere pressure, with neutrons plus gamma rays for 2 days increased the volume of the gas about 25 per cent. In a typical irradiation, 12·2 ml PH_3 (n.t.p.) yielded 15·1 ml gas (n.t.p.). This gas, which was strongly radioactive, consisted entirely of phosphine and hydrogen (Table 1). Diphosphine was not detected. Because 56 per cent of the irradiated gas was phosphine, 8·5 ml or 70 per cent of the initial phosphine remained; 3·7 ml or 30 per cent was decomposed. Hydrogen comprised 6·6 ml of the irradiated product, slightly less than 1·8 times the 3·3 ml of the phosphine that was decomposed.

The quartz tube in which the PH_3 had been irradiated was coated with a red, radioactive deposit that had a phosphorus-like odour. This deposit was insoluble in water, acids, bases, and carbon disulphide. It was stable in air for many days. It dissolved readily in bromine water and in hypochlorite solution, yielding phosphate and phosphite.

Gamma-irradiated PH_3. The irradiation of the phosphine with gamma rays for 7 days produced only a slight increase in the volume of the gas. The only detectable, gaseous component, in addition to unaltered phosphine, was hydrogen (Table 1). A very thin orange-red deposit on the walls of the quartz tube resembled that obtained by neutron plus gamma irradiation of phosphine.

Neutron irradiation of P *plus* H_2. Irradiation of 0·01 formula weight of red phosphorus in hydrogen gas at 1 atmosphere pressure did not produce a radioactive gas. Examination of the gas with the mass spectroscope did not reveal detectable quantities of phosphine or diphosphine.

Irradiation of yellow phosphorus converted the yellow form into the red modification. Likewise, volatilization of the yellow form in vacuum by the use of heat produced a deposit of the red form on the walls of the tube. As little as a milligram of the yellow phosphorus volatilized onto the walls of an evacuated quartz tube formed an opaque orange-red deposit.

DISCUSSION

The parallel migrations, shown in Fig. 1, indicate that phosphate and phosphite should be separable from each other and from hypophosphite or pyrophosphate. They also demonstrate that hypophosphite and pyrophosphite should not be separable from each other.

As no secondary zones were detected in the paper strips, large quantities of phosphorus-containing impurities could not have been present in the salts.

The results summarized in Fig. 2 demonstrate that mixtures of phosphate, phosphite, and hypophosphite are resolvable by electrochromatography and that the separated products may be identified by parallel migrations of authentic preparations, as indicated by Fig. 1. As mixtures of hypophosphite, pyrophosphate, and hypophosphate were not separable, none of these substances could have reacted rapidly in the mixture to form separable products. These different compounds that formed a single zone may be separated by migration under various conditions, as in solutions containing zinc ions, and by use of various selective reagents. These results illustrate that a basic rule of chromatography applies as well to electrochromatography. Preparations that form one migration zone may be identical, but they are not necessarily identical; preparations that form separate migration zones are different.

Table 1 summarizes the yields of the principal irradiation products without regard to their radioactivity. As the gamma irradiation accompanying the neutron bombardment was about five times the intensity of the irradiation by gamma rays alone, the yields of the alteration products resulting from neutron irradiation are much greater than those resulting from the gamma irradiation.

Figs. 3, 5, and 7 show the relative amounts of radioactivity found in various substances produced by the action of neutrons plus gamma rays on Na_2HPO_4, on Na_2HPO_3, and on NaH_2PO_2 respectively. These figures reveal the distribution of the radioactive phosphorus in the various products without regard to the quantity of the non-radioactive form of each substance present in the mixture.

Figs. 4, 6, and 8 indicate the substances formed by gamma irradiation of the phosphorus compounds. The individual products formed by gamma irradiation are similar to those formed by neutron irradiation. The relative quantities of these gamma irradiation products, revealed by neutron activation of the electrochromatograms, are in agreement with the quantities found by chemical analysis and reported in Table 1.

Fig. 3 shows that most of the radioactivity of neutron-irradiated Na_2HPO_4 was separable in the form of phosphate. Activity remaining at the starting point was due presumably to colloidal, elemental phosphorus, because this material exhibited the chemical properties of phosphorus. There is, of course, the possibility that traces of polyphosphates, some of which migrate slowly in lactic acid, may have remained at the starting point.(10,12) In acetic acid, by contrast, current investigations have shown that polyphosphates do not remain at the starting point, and with this acid, activity from the neutron irradiations did remain at the starting point, thus providing further indication of the presence of phosphorus. Two substances from the irradiated

Na_2HPO_4 separated as minor zones at either side of the phosphate zone and have yet to be identified. It is significant that substances occupying the same relative position as these two substances have been found when phosphoric acid is heated or treated with gamma rays.(12) Fig. 3 also shows that pyrophosphate and hypophosphate were not formed in detectable quantities, because there was no activity in the region (100 to 160) where both of these substances would have separated. Chemical analysis (Table 1) showed that most of the phosphate remained unchanged. From the effect of gamma rays on phosphate (Fig. 4), the products formed by neutron irradiation may have been formed, in part at least, by the action of the attendant gamma rays on the phosphate itself. When it is recalled that the gamma irradiation producing the products shown in Fig. 4 was about one-fifth of that accompanying the neutron irradiation (Fig. 3), virtually all the radioactive products formed from phosphate may have arisen from the neutron activation of the gamma-irradiation products.

Fig. 5 shows that the neutron irradiation of Na_2HPO_3 produced relatively large amounts of a variety of active products. The amount of phosphorus was greater than that formed by neutron irradiation of phosphate. Pyrophosphate was not detectable by chemical tests; hence the zone labelled H_3PO_2 in Fig. 5 is probably free of pyrophosphate. Chemical analysis (Table 1) indicates that the chemical yields of the various products were less than the radioactive yields. Specifically only 4 per cent of the phosphite had been converted to hypophosphite, but nearly half of the radioactivity appeared in the hypophosphite. Even though 89 per cent of the phosphite remained unchanged, more than half of the activity appeared in the alteration products. From these facts, the neutron reactions with Na_2HPO_3 must have resulted in a preferential conversion of phosphite into other products.

The gamma-irradiation products of Na_2HPO_3, revealed by activation of the electrochromatogram (Fig. 6), were similar to those obtained by neutron irradiation. Here, too, phosphorus was present, but pyrophosphate was not detectable. Because of the formation of chemically detectable quantities of hypophosphite, phosphate, and phosphorus by gamma rays (Table 1 and Fig. 6), some of the radioactive, neutron irradiation products must have arisen by the action of neutrons upon these gamma transformation products of the original Na_2HPO_3.

Fig. 7 shows that neutron irradiation of NaH_2PO_2 also produced a variety of radioactive products like those formed from Na_2HPO_3. About half of the radioactivity of the neutron-irradiated NaH_2PO_2 occurred in the form of phosphite, whereas chemical analysis (Table 1) indicates that only 20 per cent of the phosphorus was present as hypophosphite. This higher specific activity of the phosphite indicates that the neutron activation leads to the conversion of hypophosphite into phosphite and other products as well as to the activation of hypophosphite alone.

Gamma irradiation of Na_2HPO_2 produced many of the same substances formed by the action of neutrons plus gamma rays as shown by Fig. 8. The formation of these products by gamma rays followed by activation with neutrons must occur in the reactor. Moreover, the activation of the gamma alteration products must be secondary to the primary neutron activation reaction, particularly in the early stages of the irradiation. As the neutron irradiation proceeds, however, the phosphite formed by attendant gamma irradiation will be activated with neutrons reforming hypophosphite as indicated by Fig. 5. Some hypophosphite will also be reformed by the gamma irradiation, as indicated by Fig. 6.

With Na_2HPO_3 and NaH_2PO_2, the specific activity of the irradiation products was greater than that of the salts exposed to the radiations. From this, the neutron irradiation must be very effective in altering the salts. Conversely, the attendant gamma irradiation followed by neutron activation of the products cannot account for formation of all the radioactive alteration products.

Upon irradiation of Na_2HPO_3 and NaH_2PO_2 in vacuum in the reactor, there are at least three courses by which the radioactive products may be formed. These are (1) the action of neutrons upon the pure salts, including chemical transformations of the salts due to nuclear rearrangements; (2) the action of gamma rays upon the neutron-activated products; (3) the action of gamma rays upon the original salts followed by neutron activation of these gamma irradiation products.

When the substances submitted to neutron irradiation undergo chemical changes, as with Na_2HPO_3 and NaH_2PO_2, the radioactive products that are formed may vary with the duration of the irradiation. In the reactor, the intensity of the gamma rays and the flux and speed of the neutrons vary with the location; hence, the neutron activation products and the proportions of these products should vary with the location in the reactor as well as with the duration of the exposure.

The irradiation of phosphine (Table 1) provides an indication that this substance is not an irradiation product of the salts of phosphate, phosphite, and hypophosphite. Neither neutron nor gamma irradiation of phosphine decomposed all this gas into a mixture of phosphorus and hydrogen. Had phosphine been formed from the salts, some of it should have remained and have been detectable with the mass spectroscope or as a radioactive gas.

The neutron plus gamma decomposition of phosphine led to the formation of phosphorus and hydrogen, not to the formation of detectable quantities of the lower hydrides of phosphorus such as diphosphine and $(PH)x$. Had lower hydrides of phosphine been formed there would have been no increase in the volume of the irradiated gas, but had the phosphine been decomposed to phosphorus and hydrogen there would have been an increase in volume due to liberated hydrogen and equal to 1·5 times the volume of the phosphine decomposed. Phosphine decomposed, 3·7 ml; hydrogen found, 6·6 ml, equivalent to $1{\cdot}8 \times 3{\cdot}7$ ml.

In view of its radioactivity, the phosphine may not have undergone extensive chemical disruption upon activation with neutrons. Instead, most of the decomposition may have been caused by the gamma rays. The regeneration of phosphine by the recombination of hydrogen and radioactive phosphorus seems unlikely, because irradiation of phosphorus and hydrogen did not produce phosphine as tested by radioactivity and by the mass spectroscope.

In the neutron irradiation experiments, there was no systematic relationship between the state of oxidation of the phosphorus in the salts and its state of oxidation in the radioactive products. Irradiation of phosphate by neutrons yielded primarily phosphate. Irradiation of phosphite produced principally the more reduced hypophosphite, whereas irradiation of hypophosphite produced principally the more oxidized phosphite. Analogous effects were obtained by the action of gamma rays alone.

Irradiation effects produced by gamma rays and by gamma rays plus neutrons resemble some of the effects produced by heat, but the several effects are not identical. With heat for example, Na_2HPO_4 yields principally pyrophosphate; Na_2HPO_3 and

NaH_2PO_2 yield phosphine and phosphate. With heat there may well be an interconversion of Na_2HPO_3 and NaH_2PO_2, as is indicated for the action of gamma rays by Figs. 6 and 8 and also as is indicated for the action of neutrons by Figs. 5 and 7.

These irradiation experiments, as well as some carried out in air,(11) do not support the widely held view that a phosphorus atom receiving a neutron recoils with sufficient force upon the subsequent emission of the gamma ray to break the chemical bonds in nearly all instances. Indeed, with phosphate, most of the radioactive molecules remained in their original state of combination. With phosphite and hypophosphite about half of the active molecules remained in the original state of chemical combination, the remainder occurring in chemical species that could be formed by chemical rearrangements induced by gamma irradiation alone. With no compound, except phosphine, which is readily decomposed by gamma rays alone, was a high yield of phosphorus obtained. But even with phosphine, the neutron-irradiated gas was radioactive, indicating that it had not decomposed upon the absorption of a neutron by the phosphorus atom. With all these substances, the dissipation of the recoil nuclear energy accelerated those reactions which were promoted readily by irradiation with gamma rays alone.

The remarkable resistance of Na_2HPO_4 to irradiation in vacuum (Figs. 3 and 4) stands in sharp contrast to the earlier results, which indicate that irradiation in air yields various products.(1–12) Some of our current investigations now indicate that the formation of several products by irradiation of phosphates in air may be attributed to several distinct effects. At least three of these effects are: the action of neutrons and gamma rays upon phosphate followed by oxidation of the dissociation products, the action of gamma rays and oxygen upon the phosphate with formation of condensation products and subsequent activation of these products, and the use of non-specific chemical methods for the determination of the various activation products formed in air. These aspects of the neutron activation of other phosphorus compounds are being investigated.

Acknowledgements—The investigations summarized in this report were facilitated by Mr. LOUIS G. POBO and Mr. HERBERT L. REST, who made numerous analyses with the mass spectrometer. These studies were also aided in a material way by Dr. JOHN R. VAN WAZER, Dr. PETER G. ARVAN, and Dr. EDWARD J. GRIFFITH of Monsanto Chemical Company; by Mr. RUSSELL N. BELL and Dr. LOWELL E. NETHERTON of Victor Chemical Works; by Dr. OSCAR T. QUIMBY of Procter and Gamble Company; and by Dr. THERALD MOELLER of the University of Illinois, all of whom have contributed special phosphorus compounds for the identification of the irradiation products. The irradiations were carefully supervised by members of the staffs at the Argonne High-level Gamma-irradiation Facility and at the Argonne Reactor, and the mechanisms of the irradiation processes were discussed with Dr. E. J. HART.