## Chemical behaviour of phosphorus-32 recoils in crystalline disodium hydrogen phosphate\*

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The chemical behaviour of recoil phosphorus in inorganic crystalline systems has been repeatedly investigated (1-18) LIBBY<sup>(1)</sup> examined the radiophosphorus formed by the n,  $\gamma$  reaction in several hydrated alkali phosphates. Two fractions were distinguished, 32P which precipitated with magnesium ammonium phosphate and the residuum, oxidized with bromine and then similarly precipitated, and thought to contain phosphite. The relative insensitivity of the phosphate yield (retention) to changes in environment of the recoils, led LIBBY to conclude that the initial recoil determined the retention, subsequent reactions having no effect on the oxidation state. Later work<sup>(4,5,6,8)</sup> drew specific attention to the formation of recoil species containing more than one phosphorus, for example, pyrophosphate.

Two recent papers by Sellers et al.<sup>(10,13)</sup> reported the <sup>33</sup>P yields from irradiations in vacuo of various inorganic crystalline phosphorus compounds. Their separation technique (paper electrophoresis) gave results which indicated that in all cases virtually all the \*\*P activity was present as the parent compound.

Earlier work of BORLAND et al.<sup>(a)</sup> however, had shown that high neutron flux and ambient temperature during neutron irradiation of KH,PO, as well as thermal annealing after irradiation produced an almost complete conversion of the non-orthophosphate fraction into orthophosphate. Such annealing effects might explain the discrepancy between the work of SELLERS et al. (19,13) and the workers cited above. In addition, studies of phosphorus recoil in inorganic sulphur and chlorine compounds had suggested that in lattices containing hydrogen in any form (crystal water,  $NH_4^+$  etc.) lower oxidation states of <sup>33</sup>P should be expected.<sup>(11)</sup>

We have recently engaged in an extensive study of <sup>33</sup>P recoil reactions in crystalline systems as a function of radiation and thermal environment, i.e. temperature of bombardment, flux, neutron to gamma ray ratio, annealing conditions, and crystalline environment. Our results do not agree with those of SELLERS et al. (10,13) that the principal recoil reactions are the production of labeled parent forms. Like them, we employed paper electrophoresis separations. In Fig. 1 is shown a typical histogram (activity vs. distance along strip). The salt was anhydrous Na, HPO, bombarded at dry ice temperature<sup>†</sup> for 30 min at  $2 \times 10^{13}$  n/cm<sup>3</sup> sec, Cd ratio about 40. This salt was dissolved in ice-cold 0.1 M lactic acid, and 5-10  $\lambda$  analysed by electrophoresis on a strip of Whatman 3 MM moistened with 0.1 M lactic acid, at a voltage gradient of 80 V/cm for about 1 hr. We have determined the per cent activity, and tentatively identified the peaks labeled in the histogram, as follows:

- A tripolyphosphate, 12.2%
- B pyrophosphate, 11.7%
- C unknown, probably two species, 12.0% total
- D isohypophosphate, 27.1%
- E hypophosphate, 2.8%
- F orthophosphate, 9.3%
- G diphosphite and possibly another species, 7.7% total
- H phosphite, 8.2%
- I hypophosphite, 6.8%

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

† This bombardment was made with the sample sealed in quartz, in the presence of air. Parallel experiments with samples sealed in quartz in high vacuum gave nearly identical results.

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FIG. 1.—Electrophoresis histogram of neutron-bombarded Na<sub>3</sub>HPO<sub>4</sub>. Radioactivity vs. distance.

When the above irradiation conditions were varied by increasing the ambient temperature of bombardment our results began to approach those of SELLERS *et al.* These changes confirmed our belief that annealing during and/or after bombardment may have influenced their results.

We therefore believe that their conclusion, that "neutron irradiation of the various phosphates did not produce extensive disruption of the P—O bonds or the P—O—P linkages"<sup>(13)</sup> is unjustified. We believe, on the contrary, that the maximum probability of non-bond-rupture in crystalline phosphates is not greater than our observed orthophosphate percentage, namely 9.3 per cent, and may well be lower.

We will report our complete results on a number of such crystalline phosphorus systems shortly.

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## Diphenoxysilicon phthalocyanine<sup>(1)</sup>

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THE recent preparation of several germanium phthalocyanines<sup>(3)</sup> suggests that similar silicon phthalocyanines may exist. A successful method for the preparation of one of these diphenoxysilicon phthalocyanine, has been developed. The first step in the synthetic sequence used for this compound,

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