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THE PREPARATION OF TRI-n-BUTYL PHOSPHATE P^{32}

W. H. Baldwin and C. E. Higgins

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The Preparation of Tri-n-Butyl Phosphate[1]

by W. H. Baldwin and C. E. Higgins

(1) This document is based on work performed under Contract Number W-7405 eng 26 for the Atomic Energy Project at Oak Ridge National Laboratory.

The preparation of esters by the metathetical reaction between the silver salt of an acid and an alkyl halide, though usually considered a time-consuming and expensive method, is useful in specific applications. Since radioactive phosphorous P^{32} is readily available, in high specific activity, as orthophosphoric acid; the most direct method of synthesis of tri-n-butyl phosphate-P^{32} seemed to be through the reaction of silver phosphate with excess n-butyl bromide.

Silver phosphate has been recommended by Johnson and Nunn[2] as a primary standard for the volumetric determination of silver. The compound obtained by them was formed from silver nitrate by precipitation with excess phosphate. Earlier Lang and Kauffmann[3] had shown that attempts to precipitate phosphate completely with excess silver yielded a silver deficient compound, $Ag_3PO_4 \cdot Ag_2HPO_4$. Therefore, the first precipitate of Ag_3PO_4 was produced under the conditions recommended by Johnson and Nunn[2]. The second precipitate, produced by conditions that were calculated to remove the remaining phosphate, was analytically identical with the first precipitate but was somewhat darker in color. The yields of tri-n-butyl phosphate P^{32} from the two products were nearly identical. For synthetic purposes it appears satisfactory to precipitate

(2) Johnson, C. R. and Nunn, L. G., Jr., J. Chem. Ed. 17, 529 (1940)

(3) Lang, W. R. and Kauffmann, W. P., J. Am. Chem. Soc. 27, 1515 (1905)

the phosphate quantitatively with a slight excess of silver without sacrificing the yield of ester.

A significant amount of radioactivity remained in the solid residue from which the tri-n-butyl phosphate had been extracted. The relative amounts of incomplete reaction and side reactions were not determined. Evidence for at least one side reaction was obtained in the form of a persistent odor of butylene noted during the refluxing period; this unquestionably resulted from dehydrobromination of n-butyl bromide.

Experimental

Silver Phosphate - The procedure of Johnson and Nunn[2] was used for the preparation of the first silver phosphate precipitate. To reagent grade silver nitrate (45.4 g, 0.272 moles) dissolved in 45 ml. of distilled water was added 50 ml. of solution containing 7 ml. of 85% H_3PO_4 spiked with approximately 1 millicurie of P^{-32}[4]. The small amount of precipitate that formed was filtered,

(4) H_3PO_4* obtained from the Isotope Production Division of O.R.N.L.

washed with distilled water and discarded. Ammonium hydroxide (3M) was added to the combined filtrate and washings until the pH had reached 6. The precipitate that formed was digested for 20 hours at room temperature, filtered, washed 15 times with 10 to 20 - ml. portions of distilled water and dried in an oven at 120°C. for 16 hours to yield 37.1 g. of yellow powder (I).

A second crop (II) of silver phosphate was obtained by adding to the filtrate and washings a solution of 8.5 g. Ag NO_3 in 20 ml. distilled water and adjusting to pH6 with 3M NH_4OH. The precipitate, treated as before, dried to a dark yellow powder weighing 5.8 g.

Anal. Calc'd for Ag_3PO_4: Ag, 77.33%
Found: I Ag, 77.3%; II Ag, 77.3%
Specific Activity Found: (I), 6.8 microcuries P^{32} per millimole; (II), 6.8 microcuries P^{32} per millimole.

The filtrate and washings from this second crop contained less than 0.5% of the original beta activity employed, indicating the removal of more than 99.5% of the phosphorous.

Tri-n-butyl Phosphate - Silver phosphate (26.5 g., 0.062 mols, crop I) and 50 g. (0.36 mols) n-butyl bromide were refluxed for 2 hours (in a flask containing a magnetic stirring device) allowed to stand at room temperature overnight and refluxed again for 6 hours. During this time an odor associated with butylene was evident. The mixture in the flask was extracted with 3 portions of hot petroleum ether (30 ml. each). The combined petroleum ether extracts were washed first with an equal volume of 0.1M HCl, then with an equal volume of 0.1M NaOH, then two equal volume portions of water and dried over anhydrous sodium sulfate. After removal of the lower boiling constituents at the water pump there was obtained 9.8 g. (59% yield) of tri-n-butyl phosphate boiling between 174°C at 28 mm and 180°C at 29 mm.

Anal. Calc'd for $C_{12}H_{27}PO_4$: P, 11.63%
Found: P, 11.3%
Specific Activity Found: 6.78, 6.62 microcuries P^{32} per millimole.

A similar preparation using 4.0 g. of crop II yielded 1.4 g (55%) of tri-n-butyl phosphate boiling at 158-162° at 18 mm. pressure.