drolysis and crystallization from water, a check of the composition of the product was made by titration, using 0.1 *N* sodium hydroxide with phenolphthalein indicator. The product gave the neutralization equivalent of 142.2, against the theoretical value of 142.1.

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A New Synthesis of Phosphinic Acids

BY GENNADY M. KOSOLAPOFF

In the course of the past fifty years a great number of esters of phosphonic acids have been prepared by the reactions of active organic halides either with trialkyl phosphites (equation 1), or with dialkyl sodiophosphites (equation 2).

$$(RO)_3P + R'X \longrightarrow R'P(O)(OR)_2 + RX \qquad (1)$$

$$(RO)_2PONa + R'X \longrightarrow R'P(O)(OR)_2 + NaX \qquad (2)$$

The rather obvious extension of the first reaction to the dialkyl esters of phosphonous acids, a reaction which yields monoalkyl esters of phosphinic acids, has been used in several instances after the original work of Arbuzov,[1] following equation (3).

$$RP(OR)_2 + R'X \longrightarrow RR'P(O)OR + RX \qquad (3)$$

The main drawback of this reaction is the need for preparation of the dialkyl phosphonites, which are substances with rather disagreeable odors and which are subject to hydrolytic decomposition with great ease, thus resembling the trialkyl phosphites to a considerable degree.

The second possible synthesis of phosphinic derivatives *via* the alkali salts of monoalkyl phosphonites has been completely overlooked until this time. Since monoalkyl phosphonites may be expected to have considerable similarity to dialkyl phosphites, which have been very fruitfully employed for the syntheses of various phosphonates, the preliminary investigation of this second mode of synthesis of phosphinates was of appreciable interest. In addition, almost no useful information on the practical synthesis of monoalkyl phosphonites can be found in the literature. The meager mention that oily products obtained by partial hydrolysis of dialkyl phosphonites give analytical results which correspond to the monoesters is hardly a sufficient characterization of the class.[2]

It was felt that since phosphorus trichloride reacts smoothly with three (or more) moles of an alcohol yielding dialkyl phosphites according to equation (4)

$$PCl_3 + 3ROH \longrightarrow (RO)_2POH + RCl + 2HCl \qquad (4)$$

it should be expected that the analogous trivalent halides, *i. e.* $RPCl_2$, should similarly yield the desired monoesters of phosphonous acids, according to equation (5)

$$RPCl_2 + 2ROH \longrightarrow RP(OR)OH + RCl + HCl \qquad (5)$$

This expectation was realized without difficulty. It was noted, however, that the ethyl ester of benzenephosphonous acid is a rather unsatisfactory intermediate for these reactions; in the course of distillation this substance develops extremely foul odor of a phosphine, which makes it undesirable for any large scale syntheses. This is analogous to the behavior of diethyl phosphite mentioned earlier.[3] Once again recourse to the butyl ester solved the difficulty and monobutyl benzenephosphonite was obtained in excellent yields as an essentially odorless substance, without recourse to extreme vacuum in the distillations. As expected, the ester reacted smoothly with metallic sodium and the sodio derivative reacted with active organic halides, yielding monoalkyl esters of phosphinic acids according to equation (6).

$$RP(OR)OH + Na \longrightarrow H + RP(OR)ONa \xrightarrow{R'X} RR'P(O)OR + NaX \qquad (6)$$

The procedure does not eliminate completely the handling of malodorous substances, since the dichlorophosphines necessary for the preparation of the monoalkyl esters still must be manipulated. However, the handling of the malodorous dialkyl phosphonites is eliminated and the reaction may offer some further advantages over the scheme of reaction (3).

Experimental

Phenyldichlorophosphine was prepared by Dye's useful method[4]; the product boiled at 94° at 12 mm. and was obtained in 60–65% yields by refluxing for two hours a mixture of two moles of benzene with one mole of phosphorus trichloride and one-third of a mole of aluminum chloride. The phosphorus oxychloride variant of Dye's method was used to remove aluminum.

Addition of phenyldichlorophosphine to dry ethanol (two to five moles) with ice-water cooling, followed by vacuum distillation gave monoethyl benzenephosphonite of unsatisfactory quality; the product boiled at 98–99° at 1 mm. but possessed such fearful odor resembling that of phenylphosphine, as to be useless for practical work.

Addition of phenyldichlorophosphine to dry butanol (best mole ratio was found to be three moles of the alcohol per mole of phenyldichlorophosphine) at 5–10° with good stirring, followed by evacuation of the vessel with stirring at room temperature for two or three hours, gave upon distillation of the residual colorless liquid 70–75% yields of monobutyl benzenephosphonite, as a colorless, almost odorless liquid (the odor is reminiscent of that of dibutyl phosphite), which boiled sharply at 149° at 3 mm.; $n^{29}\mathrm{D}$ 1.5045, d^{29}_4 1.0695; *MR* found, 54.9; calcd., 54.3 (using 4.5 for atomic refractivity of phosphorus, from the average value of this constant in dialkyl phosphites; there are no data on atomic refractivities among the compounds of this series). Calculated for $C_6H_5P(OC_4H_9)OH$: P, 15.65. Found: P, 15.70, 15.75.

The ester (39.0 g.) in 200 ml. of toluene was treated with 4.4 g. of sodium and the mixture was gently warmed with stirring for four hours until hydrogen evolution ceased. The minute residuum of unreacted sodium was removed and the mixture was treated over one hour with 27.0 g. of *n*-butyl bromide. After refluxing with stirring for three hours, filtering the precipitate of sodium bromide and

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(1) Arbuzov, Dissertation, Kazan, 1914; *J. Russ. Phys.-Chem. Soc.*, **42**, 395 (1910), *C. A.*, **5**, 1397 (1911).

(2) Kohler and Michaelis, *Ber.*, **10**, 816 (1877).

(3) Kosolapoff, THIS JOURNAL, **72**, 4291 (1950).

(4) Dye, *ibid.*, **70**, 2595 (1948).

evaporating the solvent in vacuum, the product was obtained in the form of a pale yellowish viscous oil. This crude butyl phenylbutylphosphinate was refluxed with 200 ml. of concentrated hydrochloric acid for five hours with slow collection of butyl chloride at the distillation head of the hydrolysis apparatus. The residual insoluble oil was separated from the cooled mixture, dissolved in dilute sodium hydroxide and precipitated by means of hydrochloric acid. The resulting phenylbutylphosphinic acid was a viscous oil, which froze to a glass in freezing mixture; the oily character of this product was very similar to that of phenylisobutylphosphinic acid, noted by Arbuzov and Arbuzova,[5] which is an oil in the perfectly dry state and crystallizes only on partial hydration. Phenylbutylphosphinic acid, obtained in 84% yield, had the neutralization equivalent of 202, 203, against the calculated 198, after drying *in vacuo* by repeated evaporations with dry benzene. Conversion to the lead salt gave this substance in the form of colorless, insoluble powder, which contained 34.2% Pb, against calculated 34.4%.

Repetition of the reaction, using methyl iodide instead of butyl bromide, gave after three hours refluxing of the condensation mixture, followed by the above procedure, an 81% yield of methylphenylphosphinic acid, m. p. 133–134°, which agreed with the previous data for this substance.[6]

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[5] Arbuzov and Arbuzova, *J. Russ. Phys.-Chem. Soc.*, **61**, 1905 (1929).

[6] Pope and Gibson, *J. Chem. Soc.*, **101**, 740 (1912).

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Adsorption of Protactinium from Hydrochloric Acid Solutions by Anion Exchange Resins[1]

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The high extractability of protactinium from hydrochloric acid solutions by organic solvents suggested that it can form a neutral chloride complex.[2] The formula of this complex might be $PaCl_5(H_2O)_n$, in *ca.* 3*M* HCl, or a similar neutral complex with probably not more than one or two hydroxide ions per protactinium.[3]

It appeared probable that Pa(V) at a higher chloride concentration could form a negatively charged complex which might be adsorbable by anion exchange resins as were complexes of Ta(V) and Nb(V).[4] This was substantiated in a series of tracer experiments using the quaternary amine resin Dowex-1.

Experimental Procedure and Materials

Adsorption Columns.—Adsorption columns were prepared from 2 mm., i. d. Pyrex tubing, plugged with glass wool to retain the resin. The upper part of the column was in the form of a small reservoir to permit easy addition of solutions and resin. The eluent was placed in a separatory funnel which was joined to the column by means of a small ball joint. The column was filled with resin (200–230 mesh size on wet screening) to a height of 15 centimeters by adding a slurry of resin in water. The resin was washed with water and then with hydrochloric acid of the concentration which was to be used in the experiments. The elutions were carried out with flow-rates of *ca.* 0.2–0.3 ml. cm.$^{-2}$min.$^{-1}$.

Preparation of Pa^{233}.—All experiments were carried out with Pa^{233} tracer (β-emitter, $T_{1/2} = 27.4$ days)[5] which was prepared by neutron bombardment of thorium metal. After separation from thorium the Pa^{233} was found to be of high purity as shown by its decay curve.

Analysis of Elution Curves.—The β-activity of the eluent was recorded on a Brown "Electronik" strip-chart recorder by passing the solution through a thin-window flow cell which was placed near a G. M. tube. The electronic circuit contained an integrating device and the recorder was of the logarithmic type.[6] In general, the equipment was similar to that developed at the Oak Ridge National Laboratory and described by Ketelle and Boyd.[7]

Batch Experiments.—A series of batch experiments was carried out to determine the distribution coefficients of protactinium with respect to the resin as a function of hydrochloric acid concentration. For this purpose *ca.* 0.1 ml. samples of hydrochloric acid solutions containing Pa^{233} tracer were agitated with 5–20 mg. of resin for one to three days in closed tubes. Agitation was achieved either with a magnetic stirrer using a small length of 10 mil iron wire in a thin glass tube or by mounting the tubes on a vibrator.

The distribution coefficients were determined by direct beta assays of known aliquots of the solution combined with beta assays of weighed, oven-dried portions of the resin. After centrifugation the resin was placed on filter paper to remove excess solution, washed on filter paper with a 50 λ portion of hydrochloric acid of the concentration in question, blotted dry, transferred to a weighed platinum plate and weighed after drying in an oven at 110°. For the β-assays the resin was decomposed with nitric acid followed by ignition.

Results and Discussion

Distribution Coefficients.—It was found from the batch experiment that Pa^{233} is only weakly adsorbed by the anion exchange resin at hydrochloric acid concentrations less than *ca.* 4*M* and that above this concentration the adsorbability rises abruptly. The distribution coefficients (K_d) are given in Fig. 1. K_d is defined by the equation

$$K_d = P_r/P_s \qquad (1)$$

where P_r and P_s are the amounts of protactinium (*e.g.*, in counts/min.) per gram of (oven-dried) resin and per ml. of solution, respectively. It can be seen from Fig. 1 that the reproducibility of the determinations was generally poor and that the distribution coefficients had not reached equilibrium values after one day of equilibration, particularly under conditions where K_d is large. Although the values of K_d are thus only semi-quantitative, there is little doubt that protactinium under the conditions studied forms a negatively charged chloride complex.

Since the K_d values become extremely high at very high chloride concentrations, it is unlikely that the charge on the complex is more negative than minus one. The probable equilibrium in the hydrochloric acid range studied is thus

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[1] This document is based on work performed under Contract Number W-7405 Eng. 26 for the Atomic Energy Commission at Oak Ridge National Laboratory.

[2] K. A. Kraus and Q. Van Winkle, Report ORNL-239, February 1949.

[3] K. A. Kraus and A. Garen, ORNL-65 (March–May 1948) and ORNL-176 (June–August 1948).

[4] K. A. Kraus and G. E. Moore, THIS JOURNAL, **71**, 3855 (1949).

[5] Information from "Table of Isotopes," by G. T. Seaborg and I. Perlman, *Rev. Modern Phys.*, **20**, 585 (1948).

[6] The electrical circuit was prepared for us by F. W. Manning of the Instrument Division of Oak Ridge National Laboratory.

[7] B. H. Ketelle and G. E. Boyd, THIS JOURNAL, **69**, 2800 (1947).