Commercial chlorine was also purified by extensive distillation in a multiple-plate still designed by Crist and Brown.[7] The highest values of the velocity constants obtained in 24 experiments using this chlorine are shown by curves nos. 87 and 90 in the accompanying figure.[8] The corresponding constants obtained with the final crystalline product of the sublimation–crystallization process are typified by the curve no. 106. It is evident from the increased velocity of Expt. 106 that the latter chlorine is purer than that obtained by distillation.

As a further check on our results, measurements of velocity constants were made using the chlorine purified by distillation in the 240 cm. column still to which amounts of air corresponding to pressures of 1.3, 1.1, 0.6, and 0.1 mm. were added. The results thus obtained are shown in curves 86, 88, 89, and 92, respectively. These curves show an increased velocity over nos. 87 and 90 as well as the typical oxygen induction period due to the added air. Since it is difficult to account for the increase in reaction rate upon the addition of an impurity (air) and since addition of air to reaction mixtures containing the purest chlorine always resulted in a lowered rate,[3] this is further evidence that an impurity still exists in the chlorine prepared by distillation.

The successful purification of chlorine by the sublimation–crystallization process was accomplished using chlorine from several sources. It is believed that this method can be applied wherever small amounts of extremely pure chlorine are needed.

Summary

A low-pressure sublimation–crystallization process for the rigorous purification of chlorine depending upon a 17° gradient close to the melting point of chlorine is described.

A method for the detection of traces of impurities in the chlorine utilizing the photochemical formation of phosgene is reported.

NEW YORK, N. Y. RECEIVED SEPTEMBER 18, 1940

---

[7] The design of the still together with a detailed method of operation will be published by Crist and Brown. It consisted essentially of a two-liter boiler and a 240 cm. packed column.

[8] Weber (Columbia Dissertation, 1933) found that commercial chlorine purified merely by passage in succession through a water scrubber, sulfuric acid and a heater maintained at 350°, often gave a product exhibiting the rate of phosgene formation normal for the very purest chlorine. In other cases he found that several distillations were necessary and sufficient to produce the same results. We attempted to use this method for the purification of chlorine from seven tanks but in no case did the resulting chlorine give the high velocity constants characteristic of the purest chlorine.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Attempted Exchange of Radiophosphorus between Ortho-, Pyro- and Metaphosphoric Acids

BY D. E. HULL

Several attempts have been made to discover an exchange of radioactive phosphorus between acids of phosphorus in different oxidation states, but so far no case has been found in which such exchange occurs.[1,2] Phosphorus in the +5 oxidation state forms several acids differing in the degree of hydration, the most important of which are orthophosphoric acid, pyrophosphoric acid, and metaphosphoric acid. It would be of interest to know whether any exchange of phosphorus takes place between these acids in aqueous solution under various conditions of concentration, acidity, and temperature. This paper is to report a few exploratory experiments carried out in dilute solutions.

In aqueous solution the ortho acid is the stable form; both the meta and the pyro acids change to the ortho. The change is fairly slow at room temperature, requiring something less than one day for half conversion of the meta acid, and about four days for the pyro.[3] The rate is accelerated by an increase in concentration, acidity, or temperature. The pyro acid is ordinarily an intermediate in the conversion of the meta acid to ortho. In order that these reactions might not obscure the results of an attempted exchange, the more hydrated acid was the one marked with the radioactive indicator in each case, and the less hydrated acid was used in the inactive form.

We may postulate two mechanisms by which an exchange could be effected between the acids of +5 phosphorus. First, reactions in which water is reversibly split off and taken up, thus

$$H_3PO_4 \rightleftarrows HPO_3 + H_2O \tag{1a}$$

$$2H_3PO_4 \rightleftarrows H_4P_2O_7 + H_2O \tag{1b}$$

$$H_4P_2O_7 \rightleftarrows 2HPO_3 + H_2O \tag{1c}$$

Secondly, a reaction whereby pyrophosphoric acid dissociates reversibly into the ortho and meta acids

$$H_4P_2O_7 \rightleftarrows HPO_3 + H_3PO_4 \qquad \text{(2}$$

---

[1] Perrier and Segre, *Ricerca sci.*, **9**, 638 (1938).

[2] Wilson, THIS JOURNAL, **60**, 2697 (1938).

[3] Durgin, Lum and Malowan, *Trans. Am Inst. Chem. Engs.*, **33**, 643 (1937).

assuming the pyro acid to have a symmetrical arrangement of the phosphorus atoms, as is known to be the case in its salts.[4]

Since reactions 1a, b, and c are known to proceed from right to left, the test for exchange is essentially a test of the reversibility of these reactions. There is evidence for the existence of an equilibrium represented by equation 2 in concentrated ("anhydrous") phosphoric acid,[5] but there are not sufficient data for extrapolating this result to dilute solutions.

Preparation of Materials.—Radiophosphoric acid was prepared with P^{32} (14.3 days half-life) from three different sources:

(1) A 2-liter flask of carbon disulfide containing 0.001 mole of dissolved yellow phosphorus was irradiated with neutrons from a Rn–Be source placed in the center of the flask. Then liquid bromine was added drop by drop to the solution until an excess was indicated by the color, and the radiophosphoric acid was extracted with water. The aqueous extract was evaporated to dryness and weighed. Sufficient standard phosphoric acid was added to make the desired quantity, then the whole was diluted to 100 cc. A 100-millicurie radon source will produce during ten days of exposure (the optimum time) enough radiophosphorus to give a counting rate of 75 per sec. under the conditions of measurement described below. (Extraction of radiophosphorus from the carbon disulfide with 6 *N* nitric acid was found to give a poor yield. 16 *N* nitric acid gives a better yield, but also produces a considerable quantity of sulfuric acid by oxidation of the carbon disulfide. Even after extraction with concentrated nitric acid a considerable fraction of the radiophosphorus remains in the carbon disulfide, as can be shown by subsequent treatment with bromine.)

(2) Calcium metaphosphate was bombarded with deuterons from the electrostatic generator in the Physics Department.[6] Pure radiophosphoric acid was prepared from this by a method described elsewhere.[7]

(3) Disodium phosphate was bombarded with deuterons from a cyclotron.[6] The concentration of radiophosphorus in this sample was much greater than in those prepared by the other methods, and in some earlier experiments phosphoric acid was labeled with radioactive phosphorus by merely adding a convenient quantity of the salt (less than 1 mole per cent.). Subsequent tests showed that a small fraction of the radiophosphorus in this sample was in the form of phosphorous acid. Therefore, the remainder of the sample was treated with bromine and converted into pure phosphoric acid for later experiments. Those experiments in which the phosphorous acid was present gave results which differed in no way from the others.

Metaphosphoric acid was prepared from 85% U. S. P. phosphoric acid by evaporating the latter and finally heating it to a dull red heat for a few minutes. This was freshly dissolved in water for each set of experiments in order to keep the amount of orthophosphoric acid to a minimum.

Pyrophosphoric acid was prepared by heating 85% phosphoric acid to 240°. This was also freshly dissolved for the various experiments.

Ortho- and Metaphosphoric Acids.—The desired quantities of metaphosphoric acid and radio-orthophosphoric acid were mixed together in a convenient volume of water and allowed to stand for a stated interval of time. At the end of the time allowed for reaction, barium chloride solution was added to precipitate barium metaphosphate, which was filtered. To the filtrate ammonium hydroxide was added to precipitate barium orthophosphate.

Filtration was carried on by suction through a 5.5-cm. filter in a Büchner funnel. The precipitate was washed several times with water, then twice with 95% ethyl alcohol, and finally twice with ether. After the filter paper and precipitate were dried, they were carefully removed from the funnel, and then wet all over with 1 cc. of a 2% solution of cellulose acetate in acetone, applied with a dropper. The evaporation of the acetone, accomplished over a hot plate, left a thin film covering the precipitate and holding it firmly in place.

In some experiments the procedure was varied by heating the reaction mixture by immersing a test-tube containing it in a beaker of boiling water for the desired time, then quickly transferring it to a stream of cold water. In others, an excess of sodium hydroxide was added to the reaction mixture before heating it. In these cases the solution was restored to its original *p*H by titration with *N* hydrochloric acid using tropeoline 00 as an indicator, before adding the barium chloride.

Ortho- and Pyrophosphoric Acids.—Reaction mixtures with inactive pyrophosphoric acid and labeled orthophosphoric acid were prepared and treated as in the preceding section. In this case separation was effected by adding 5 cc. of a buffer solution 3.5 *M* in sodium acetate and 1.4 *M* in acetic acid, then adding dropwise 1 cc. of *M* cadmium nitrate. Under these conditions cadmium pyrophosphate is precipitated. After filtering this out, calcium chloride and ammonium hydroxide were added to precipitate calcium orthophosphate. These precipitates were prepared for measurement in the same way as before.

(Zinc acetate is generally recommended as a reagent for the separation of pyrophosphoric acid from other phosphoric acids; but it was found in these experiments that not only is the precipitation of zinc pyrophosphate incomplete, but large quantities of zinc orthophosphate are coprecipitated. The use of Cd^{++} in a properly buffered solution as described was found to give a much sharper separation.)

Pyro- and Metaphosphoric Acids.—Labeled pyrophosphoric acid was prepared by evaporating a sample of radiophosphoric acid in a test-tube partially immersed in a mercury bath, finally raising the temperature to 250°. After cooling, the resulting radio-pyrophosphoric acid was dissolved in water at room temperature, and inactive metaphosphoric acid was added to test the exchange. Separation of these two acids was accomplished by the procedure of adding barium chloride and ammonium hydroxide, respectively, to precipitate in turn barium metaphosphate and barium pyrophosphate. These were prepared for measurement in the usual way.

---

(4) Levi and Peyronel, *Z. Krist.*, **92**, 190 (1935).

(5) Gerber and Miles, *Ind. Eng. Chem., Anal. Ed.*, **10**, 519 (1938).

(6) These active samples were obtained through the courtesy of Professor J. H. Williams of the Physics Department.

(7) Hull and Williams, *Rev. Sci. Instruments*, **11**, 299 (1940).

Measurements.—All measurements of activity were made by wrapping the cellulose coated filter paper around a cylindrical counter of the glass-wall type. The paper was held in place by a rubber band. The filter paper was always located in the same position on the counter, a necessary precaution because of the irregularities in the cylinder inherent in a counter of this type construction. Measurements of several equal portions of a radiophosphoric acid solution, all precipitated and filtered in the same way, show that a reproducibility of 1% can be attained by this technique. The counter was used in a Neher-Harper circuit with a resolving time of 0.0008 sec.[8] so that counting losses at the greatest counting speeds observed in this experiment were less than 2%. Since the results are consistently negative, no corrections have been made for this, nor for self-absorption of β-rays in the various samples. Each activity was measured over an interval of about ten minutes.

The results of the experiments are shown in the accompanying tables. The pH values were calculated from the known dissociation constants of the acids. The probable errors in the final ratios were calculated from the statistical fluctuations in the observed counting rates. For example, in experiment 6

$$\frac{(P_2O_7)}{(PO_4)} = \frac{(0.97 \pm 0.03) - (0.88 \pm 0.03)}{(19.40 \pm 0.12) - (0.88 \pm 0.03)} = \frac{0.09 \pm 0.04}{18.52 \pm 0.12} = 0.005 \pm 0.002$$

TABLE I

ORTHO AND META ACIDS

Expt. no.	1	2	3	4
Reaction Mixture:				
$H_3P^*O_4$, micromoles	200	200	100	100
HPO_3, micromoles	100	200	100	100
NaOH, micromoles	...	...	...	1050
Volume, cc.	11.0	12.0	11.0	21.0
pH	2.0	2.0	2.0	12.5
Temperature, °C.	29	*ca.* 100	21	*ca.* 100
Time, min.	20.0	2.0	2.0	3.0
Measurements:				
Background, counts/sec.	0.62	0.64	0.73	0.59
Activity of $Ba(PO_3)_2$	0.62	0.62	0.72	0.62
Activity of $Ba_3(PO_4)_2$	11.02	10.59	19.76	18.51
Ratio of corrected activities, $(PO_3)/(PO_4)$	0.000	−0.002	0.000	0.002
Probable error in ratio	±0.003	±0.003	±0.002	±0.002

TABLE II

ORTHO AND PYRO ACIDS

Expt. no.	5	6	7	8
Reaction Mixture:				
$H_3P^*O_4$, micromoles	100	200	200	200
$H_4P_2O_7$, micromoles	50	100	100	100
NaOH, micromoles	...	...	1050	1050
Volume, cc.	11.5	12.0	22.0	22.0
pH	2.2	2.0	12.2	12.2
Temperature, °C.	26	100	25	*ca.* 100
Time, min.	1.0	30.0	100	3.0
Measurements:				
Background, counts/sec.	0.53	0.88	0.86	0.86
Activity of $Cd_2P_2O_7$	0.65	0.97	1.26	1.24
Activity of $Ca_3(PO_4)_2$	7.52	19.40	20.46	19.45
Ratio of corrected activities, $(P_2O_7)/(PO_4)$	0.017	0.005	0.020	0.020
Probable error in ratio	±0.002	±0.002	±0.002	±0.002

TABLE III

PYRO AND META ACIDS

Expt. no.	9	10
Reaction Mixture:		
$H_4P_2{}^*O_7$, micromoles	50	50
HPO_3, micromoles	100	100
Volume, cc.	11.0	11.0
pH	2.3	2.3
Temperature, °C.	27	*ca.* 100
Time, min.	0.5	1.5
Measurements:		
Background, counts/sec.	0.56	0.63
Activity of $Ba(PO_3)_2$	.59	.58
Activity of $Ba_2P_2O_7$	3.90	3.02
Ratio of corrected activities, $(PO_3)/(P_2O_7)$	0.009	−0.021
Probable error in ratio	± .006	± .013

Discussion of Results.—The absence of any activity in the metaphosphoric acid in the experiments listed in Tables I and III is evidence for the lack of exchange between this acid and the ortho and pyro acids, respectively, and also for the completeness of separation of metaphosphoric acid from the other acids. The small activity found in the pyrophosphoric acid in Expts. 5–8 appears to be the result, not of exchange but of a small coprecipitation of orthophosphate with pyrophosphate, because the activity does not increase with longer standing or higher temperature of the reaction mixture. Experiments 2, 4, 6, and 10 were carried out under such conditions that a large fraction of the inactive acid was hydrated during the experiment,

---

(8) Hull, *Rev. Sci. Instruments*, **11**, 404 (1940).

but even under these conditions there is no evidence for the reverse reaction. It therefore appears that none of the reactions proposed as offering a mechanism for the exchange of phosphorus between these compounds proceeds at an appreciable rate in dilute solution.

From data which have been published on the rates of hydration of pyro- and metaphosphoric acids, and present data on the reverse reactions, an upper limit can be placed on the equilibrium constants for equations 1a, b, and c. The data of Sabatier[9] on the rate of hydration of metaphosphoric acid at different temperatures and concentrations can be used to estimate the rate k'_a of equation 1a from right to left. He publishes data on the value of k in the equation $c = c_0 10^{-kt}$ for the exponential decay of the concentration of metaphosphoric acid as a function of the initial concentration c_0 over a range from 0.195 M to 1.17M, and as a function of the temperature from 0 to 80°. These data have been extrapolated to the conditions of experiment 2 ($c_0 = 0.017\ M$, $T = 100°$). The temperature extrapolation was made by the usual plot of log k *vs.* $1/T$, and is probably reliable. Extrapolation to the desired concentration was made by a straight line plot of log k *vs.* log c_0, which is found to represent Sabatier's data fairly well, the slope being reasonably independent of the temperature. This extrapolation is over a wider range, and is much more uncertain. In this way a value of $k'_a = 1.7$ hr.$^{-1}$ (to the base e) is obtained. Taking as the upper limit on k_a for the forward reaction the probable error in the measurement of the amount of orthophosphoric acid transformed to metaphosphoric acid in experiment 2, we get $k_a < 0.003 \times (60/2) = 0.09$ hr.$^{-1}$. From these two values for the reaction rates, we deduce an upper limit for the equilibrium constant $K_a < 0.09/1.7 = 0.05$.

From data published by Abbot[10] on the exponential decay of the concentration of pyrophosphoric acid at initial concentrations of 0.0125 M and 0.05 M, and at temperatures of 75 and 100°, a similar extrapolation to the conditions of experiment 6 ($c_0 = 0.008\ M$, $T = 100°$) gives a value of $k'_b = 1.8$ hr.$^{-1}$. For the forward reaction (without taking any account of the stoichiometric relations, in view of the obscurity still attached to the mechanism) we find from the data of experiment 6, $k_b < 0.005 \times (60/30) = 0.01$. Thus the equilibrium constant $K_b < 0.01/1.8 = 0.006$.

A similar calculation on the results of experiment 10 gives a limit for the equilibrium constant in equation 1c, $K_c < 0.2$.

Summary

An attempt was made to detect the exchange of radioactive phosphorus between ortho-, pyro- and metaphosphoric acids in dilute aqueous solutions. No exchange is found either in acid or alkaline solutions at temperatures from 20 to 100°.

Reactions which might be expected to effect such an exchange are discussed, and limits on the equilibrium constants for such reactions are deduced from the experimental results.

The completeness of separation of meta from the other phosphoric acids by use of Ba^{++}, and a practically complete separation of pyro from orthophosphoric acid by use of Cd^{++}, are demonstrated by means of the radioactive indicator method.

MINNEAPOLIS, MINNEOSTA

RECEIVED DECEMBER 21, 1940

---

[9] Sabatier, *Ann. chim. phys.*, [6] **18**, 409 (1889).

[10] Abbot, THIS JOURNAL, **31**, 763 (1909).