Hydrolysis Rates of Solutions of Pyrophosphoric Acid

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Hydrolysis rates were determined at 30.0° for solutions of pyrophosphoric acid of various concentrations and at 60.0° for a 0.1 molal solution.

PYROPHOSPHORIC ACID is the only member of the family of condensed phosphoric acids which may be obtained as a pure, crystalline solid. Hence, its rate of hydrolysis as a function of concentration and temperature has been determined conveniently in solutions prepared by dissolution of the acid in water.

Pyrophosphoric acid was prepared essentially as described by Malowan (*6*). It contained only 0.3% orthophosphoric acid and negligible amounts of higher phosphoric acids. Hydrolysis rates were measured at 30.0° for various concentrations of pyrophosphoric acid and also at 60.0° for a 0.1 molal solution. Solutions for 30° hydrolyses were prepared from distilled water, initially at 10°, and the acid in a blender. Zero time was taken as the time of mixing. Dissolution was accomplished in a few minutes and solutions were transferred to large test tubes which were placed in a water bath maintained at 30 ± 0.1°. For the 60° hydrolysis, water for the preparation of the solution was initially at 65° and the bath was maintained at 60 ± 0.1°. Aliquots were withdrawn by pipette and titrated for total phosphorus and phosphorus as orthophosphoric acid according to the method of Gerber and Miles (*4*). The initial concentration of pyrophosphoric acid determined by a titration within minutes of the dissolution step agreed within experimental error with the value calculated from the weights of acid and water used, thus ruling out any fast excessive hydrolysis during the dissolution step.

Data are summarized in Table I. The slight pH increase observed in certain hydrolyses would be expected since orthophosphoric acid is a slightly weaker acid than pyrophosphoric acid. In each case a gradually decreasing rate of formation of orthophosphoric acid was evident from the curved plots of either $C_{H_4P_2O_7}$ or log $C_{H_4P_2O_7}$ *vs.* time. One-quarter-, half, and three-quarter-lives presented in Table I were determined with an estimated uncertainty varying from ±2 to ±5 per cent by interpolation of these curves. The decreasing rate is reflected by the quotient $(t_{3/4} - t_{1/2})/t_{1/2}$. Alternatively, the slope of a tangent to the log C *vs.* time plot may be taken for calculation of the rate constant for a given time and pH.

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Table I. Hydrolysis of Pyrophosphoric Acid

Molality	Temp., °C.	pH, t_0 to $t_{3/4}$	$t_{1/4}$, Hr.	$t_{1/2}$, Hr.	$t_{3/4}$, Hr.
0.100	30.0	1.2 to 1.4	67	185	458
0.100[a]	30.0	0.95 ± 0.05	102	270	670
0.100	60.0	1.8 to 2.1	2.7	7.7	18.5
0.505	30.0	0.6 to 0.8	15.5	39	108
2.02	30.0	0.15 ± 0.05	3.5	9.8	25.7
5.58	30.0	<0 to <0	0.77	2.37	6.5

[a] In the presence of 2 molal $NaNO_3$.

Pyrophosphate hydrolysis kinetics has been studied extensively in recent years and interpretation of results has evoked much interest. The hydrolysis follows pseudo-first-order kinetics at constant temperature, pH and ionic strength (*1, 2, 3, 7–9*). The main purpose of this work is in the presentation of experimental results for solutions prepared directly from pyrophosphoric acid and water. The results for 0.1 molal solutions at 30° and 60° agree closely with the earlier work of Kiehl and Claussen (*5*) for 0.125*M* $H_4P_2O_7$ formed in solution from $Na_4P_2O_7$ and HCl. It is concluded that dilute to moderately concentrated solutions of pyrophosphoric acid are fairly stable toward hydrolysis.

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