TABLE I

Salt	Procedure	Form and m.p.	Metal, % Calcd.	Metal, % Found
$(Ph_2PO_2)_2Cu$	A	Blue needles	12.77	12.78
$(Bu_2PO_2)_2Cu$	A	Green needles	15.20	15.3
$[(C_{10}H_{21})_2PO_2]_2Cu$	A	Blue needles, m.p. 94°	8.42	8.5
$(Ph_2PO_2)_2Ba$	B	Needles	22.3 for $2.5H_2O$	22.26
$(Bu_2PO_2)_2Ba$	B	Needles	27.93	27.85
$[(p\text{-}ClC_6H_4)_2PO_2]_2Ba$	B	Needles	19.35	19.41
$[(C_{10}H_{21})_2PO_2]_2Ba$	B	Needles, m.p. under 100°	16.58	15.8
$(Ph_2PO_2)_2Mg$	B	Needles	5.3	5.4
$(Bu_2PO_2)_2Mg$	B	Needles	6.42	6.55
$[(C_{10}H_{21})_2PO_2]_2Mg$	C	Needles, m.p. 82–83°	3.4	3.1
$[(p\text{-}ClC_6H_4)_2PO_2]_2Mg$	B	Needles	4.07	4.3
$(Ph_2PO_2)_2Ca$	B	Needles	8.4	8.0
$(Bu_2PO_2)_2Ca$	B	Needles	10.16	10.3
$[(C_{10}H_{21})_2PO_2]_2Ca$	B	Waxy needles	5.47	5.53
$[(p\text{-}ClC_6H_4)_2PO_2]_2Ca$	B	Needles	6.54	6.50
$(Bu_2PO_2)_2Pb$	D	Needles	36.89	36.75
$[(p\text{-}ClC_6H_4)_3PO_2]_2Pb$	D	Needles	26.58	26.58
$[(C_{10}H_{21})_2PO_2]_2Pb$	D	Needles	23.07	22.92
$(Ph_2PO_2)_2Pb$	D	Needles	32.2	42.7[a]
$(Ph_2PO_2)_2Pb$	A	Powder	32.2	34.15

[a] The product obtained was substantially the basic salt. Procedure A gave a product that had an admixture of the basic salt, which could not be removed by repeated crystallization.

bilities in water of the magnesium, barium and calcium salts of dibutylphosphinic acid and of the magnesium salt of diphenylphosphinic acid. The high solubility of barium dibutylphosphinate in 96% ethanol, and that of copper di-*n*-decylphosphinate, barium di-*n*-decylphosphinate, magnesium di-*n*-butyl- and di-*n*-decylphosphinates in warm benzene should be noted. The tendency of the salts of barium, calcium and magnesium to have higher solubility in cold water than in hot water is also of interest. The inverse solubility–temperature relation is also seen in alcoholic solutions of magnesium and calcium diphenylphosphinates and magnesium bis-*p*-chlorophenylphosphinate.

Experimental Part

Preparation of the Salts.—The following typical procedures were used.

Procedure A.—Five grams of diphenylphosphinic acid, suspended in 50 ml. of water, was neutralized with *N* sodium hydroxide (phenolphthalein indicator). The filtered solution was treated with a slight excess (0.012 mole) of *M* cupric chloride. The product, in the form of light-blue tiny needles, was washed with water and ethanol, and dried in air.

The procedure failed with the bis-*p*-chlorophenylphosphinic acid. The product consisted of two components neither of which had the properties of the desired salt. The free acid could not be regenerated from it by treatment with mineral acids, indicating a formation of a complex at the halogen atom.

Procedure B.—Five grams of diphenylphosphinic acid, suspended in 50 ml. of water, was neutralized directly with *M* barium hydroxide. The filtered solution was evaporated to dryness and the residue was crystallized from 96% ethanol. The air-dried product contains 2.5 molecules of water which are lost by heating in vacuum at 120°; the anhydrous product is extremely hygroscopic.

Procedure C.—An intimate mixture of 5 g. of di-*n*-decylphosphinic acid (m.p. 87–88°) with 1.5 g. of magnesium acetate tetrahydrate was heated under an infrared lamp until all odor of the eliminated acetic acid was removed. The product was washed with hot water, followed by ethanol. It forms tiny needles, m.p. 82–83°.

Procedure D.—A mixture of five grams of di-*n*-butylphosphinic acid and 3.4 g. of lead oxide was refluxed in 200 ml. of xylene with collection of the evolved water in a Starke–Dean moisture trap. The reaction was complete in 30 minutes. The hot solution was filtered rapidly and cooled. The product precipitated in the form of felted needles which were recrystallized from water. The product was anhydrous after air-drying.

TABLE II

SOLUBILITY OF THE SALTS, IN GRAMS PER 100 ML. OF SOLUTION

Salt	Water 25°	Water 35°	Water 45°	96% Ethanol 25°	96% Ethanol 35°	96% Ethanol 45°	Benzene 25°	Benzene 35°	Benzene 45°
$(Bu_2PO_2)_2Pb$	0.0654	0.066	0.0662	0.452	0.542	0.588	0.032	0.030	0.158
$[(ClC_6H_4)_2PO_2]_2Pb$	.0076	.0178	.0216	.068	.084	.112	.094	.092	.090
$[(C_{10}H_{21})_2PO_2]_2Pb$	.0008	.0012	.0016	.036	.042	.056	.034	.052	.572
$(Ph_2PO_2)_2Cu$	.0400	.0424	.0430	.006	.020	.000	.000	.000	.000
$(Bu_2PO_2)_2Cu$	.0172	.0186	.0220	.246	.250	.324	.080	.248	.816
$[(C_{10}H_{21})_2PO_2]_2Cu$	.0034	.0038	.0039	.026	.060	.108	.110	2.758	25.418
$(Ph_2PO_2)_2Ba$	.112	.111	.110	.112	.114	.152	.138	.198	0.240
$(Bu_2PO_2)_2Ba$	Over 188	Not detd.		13.38	14.05	21.24	.000	.000	.000
$[(ClC_6H_4)_3PO_2]_2Ba$	1.128	1.056	1.018	0.430	0.538	0.916	.018	.022	.024
$[(C_{10}H_{21})_1PO_2]_2Ba$	0.0036	0.0016	0.001	.326	.327	0.334	.000	4.208	4.366
$(Ph_2PO_2)_2Mg$	3.554	3.350	2.616	.290	.288	....	.000	0.000	0.000
$(Bu_2PO_2)_2Mg$	6.570	4.714	3.168	.178	.266	0.728	.168	2.438	Gel.
$[(ClC_6H_4)_2PO_2]_2Mg$	0.382	0.342	0.302	.400	.286	.196	.006	0.002	Gel.
$[(C_{10}H_{21})_2PO_2]_2Mg$	.0012	.0010	.0008	.030	.048	.076	.144	.200	15.774
$(Ph_2PO_2)_2Ca$	.704	.698	.694	1.224	1.196	1.199	.000	.004	0.004
$(Bu_2PO_2)_2Ca$	4.636	4.362	4.318	0.314	0.418	0.712	.002	.002	.002
$[(ClC_7H_4)_2PO_2]_2Ca$	0.114	0.114	0.114	.636	.760	2.970	.118	.180	.334
$[(C_{10}H_{21})_1PO_2]_2Ca$	0.0029	0.0036	0.0036	.024	.038	0.062	.028	.066	080

This procedure when used with diphenylphosphinic acid gave a product that was largely the basic salt, containing 42.74% of lead.

The procedures used in the preparation and the properties of the products are listed in Table I.

AUBURN, ALA.

Rates of Hydrolysis of Fructose-6-phosphoric Acid[1]

BY S. L. FRIESS

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In studies concerned with the acid-catalyzed cleavage of a terminal phosphate group from the

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adenosine triphosphate molecule, it was essential to have some estimate of the magnitude of the rate for the competing, non-terminal hydrolysis reaction at the ribose–phosphorus linkage. For this purpose, fructose-6-phosphoric acid (FPA) was selected as an available model compound to yield order of magnitude information on the hydrolysis rate of the primary sugar hydroxyl–phosphorus grouping.

Previous reports[2,3] on the hydrolysis of fructose mono- and diphosphates have indicated a greater lability toward aqueous hydrochloric acid of the 1-phosphate linkage as compared to the 6-grouping,[2] and a rate constant[3] for the relatively rapid hydrolysis of fructose-1-phosphate (in 0.1 *N* HCl at 100°) amounting to 1×10^{-2} sec.$^{-1}$. In the present work, the 6-phosphate ester hydrolysis was carried out under somewhat milder conditions, closely approximating those used in previous kinetic work[4] on the acid-catalyzed hydrolysis of triphosphoric and pyrophosphoric acids; reaction temperatures of 40 and 50° were employed, and at each temperature hydrolysis rates were determined at two levels of acidity. No additional inert salt was present in these rate runs beyond that introduced in the sample preparation procedure.

The stoichiometric hydrolysis reaction

$$C_5H_9O_5\text{–}CH_2OPO_3H_2 + H_2O \longrightarrow C_6H_{12}O_6 + H_3PO_4$$

was followed by colorimetric evaluation of inorganic phosphate evolved, using the method of Lowry and Lopez.[5] First-order rate constants were calculated for the exceedingly slow hydrolyses over roughly the first several per cent. of each reaction, corresponding to a total reaction time of about 10 days. Values for these constants and their observed deviations are summarized in Table I.

TABLE I

ACID-CATALYZED HYDROLYSIS OF FRUCTOSE-6-PHOSPHORIC ACID (FPA)

Run	Reaction temperature,[a] °C.	Initial concentrations Acid catalyst, *N*	FPA, *M*	k_1, sec.$^{-1}$ × 10^8
1	39.93	H_2SO_4, 0.0247	0.0210	1.09 ± 0.06
2	39.93	H_2SO_4, .0914	.0210	1.75 ± .07
3	50.23	H_2SO_4, .0247	.0210	4.11 ± .10
4	50.23	H_2SO_4, .0914	.0210	6.52 ± .47
5	39.93	HCl, .0853	.0210	1.26 ± .08

[a] Temperatures held constant to ±0.02°.

The data of Table I indicate first of all that the hydrolysis is markedly slower than that of the 1-phosphate ester, and subject to acid catalysis (compare runs 1 and 2, 3 and 4). Also, comparison of the rate constants for FPA with those for hydrolysis of pyrophosphoric and triphosphoric acids[4] under comparable conditions of acidity and temperature reveals that cleavage of the phosphate entity from FPA *is slower by a factor of 10^2 to 10^3* than hydrolytic cleavage of a single phosphate group from either polyphosphate species. This fact lends considerable support to the probability that acid-catalyzed hydrolysis of adenosine triphosphate under equivalent conditions will proceed largely by cleavage at the terminal phosphate grouping, without a significant contribution from slower hydrolysis at the internal sugar–phosphorus bond.

In this connection, it is also of considerable interest that both the acid-catalyzed[4,6] and enzymatically-catalyzed[7] hydrolysis of the related polyphosphate, triphosphoric acid, involve cleavage of a terminal phosphate residue.

Further, the data of Table I permit a rough comparison of the temperature coefficients for the hydrolysis of FPA at relatively low (0.025 *N*) and high (0.09 *N*) levels of added acid. For the temperature interval employed, both low acidity (runs 1 and 3) and high acidity (runs 2 and 4) determinations lead to virtually the *same* temperature coefficient for k_1, *i.e.*, a factor of about 3.7 for 10.3°. This would imply that both the catalyzed and uncatalyzed contributions to observed k_1 values have the same temperature dependence.

As a final observation, the results of run 5 employing HCl as catalyst (compared to 1 and 2 using H_2SO_4) point to the relative insensitivity of the hydrolysis to the nature of the strong acid used as catalyst.

Experimental

The barium salt of fructose-6-phosphoric acid was used directly as supplied by the Nutritional Biochemicals Corporation. Analyses for total hydrolyzable phosphate and for barium ion indicated a maximum purity of 95.5% with respect to barium fructose phosphate. Triply distilled water was used in all rate determinations.

In a given rate run, a weighed portion of barium salt was dissolved completely in about 25 ml. of water, giving a pale yellow solution. To this was added the equivalent quantity of sodium sulfate, in small portions with continual stirring. The required amount of a standard solution of acid catalyst was then added by pipet, with stirring. After standing in the cold for about five minutes, the mixture was filtered directly into the 50-ml. volumetric flask used as the reaction vessel, with about 15 ml. of water being used in the transfer and subsequent washing. The solution was then placed in the constant temperature bath, allowed to come to temperature, and made to volume with preheated water.

Aliquots (2 ml.) of reaction mixture were withdrawn at intervals of roughly 24 hours, delivered into about 40 ml. of water containing 0.4 millimole of sodium acetate, made to 50 ml., and finally analyzed colorimetrically[5] for inorganic phosphate. Concentrations of FPA were calculated from initial values and the subsequent analytical values for phosphate.

In general, one to two days of reaction time was allowed to elapse before the initial phosphate determination was made, to ensure the completion of an induction period noted occasionally.

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The Electrolytic Preparation of Periodate Oxystarch

BY WILLIAM DVONCH AND C. L. MEHLTRETTER

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The usefulness of periodic acid in preparative work is limited by its high cost. Since periodic acid is prepared electrolytically,[1,2] it seemed probable

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