phenol. However, certain conclusions are apparent from the data here presented.

(1) The tetramethylol dihydroxydiphenylmethane is formed in alkaline solution by reaction between two molecules of trimethylolphenol, with loss of the elements of formaldehyde and water. Under our conditions, formation by reaction between trimethylolphenol and the open *para* position of 2,6-dimethylolphenol does not occur. In Figs. 2 and 4, the 2,6-dimethylolphenol is always gone from the system before formation of tetramethylol "ditan" is apparent. Addition of 2,6-dimethylolphenol to a solution of 2,4,6-trimethylolphenol in alkali was unexpectedly found to retard tetramethylol "ditan" formation, though it did not completely prevent it. When the 2,6-dimethylolphenol was removed from the solution by reaction with added formaldehyde, "ditan" formation again progressed normally. An explanation for this retarding effect is not yet apparent.

(2) The conversion of trimethylolphenol to tetramethyloldihydroxydiphenylmethane appears to be a first-order reaction dependent on concentration of trimethylolphenol. Using data from the latter parts of Experiments 1 and 5 (where only trimethylolphenol and the "ditan" remain in the system), we find that within the concentration range studied (0.7–1.7 moles/l.), a plot of logarithm of concentration of trimethylolphenol against time gives a straight line. The first-order constant determined from the slope of this line is found in both instances to be of the order of 4.4×10^{-7} sec.$^{-1}$.

EAST PITTSBURGH, PENNA.

[CONTRIBUTION NO. 1204 FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Heat of Hydrolysis of Inorganic Pyrophosphate[1]

BY NELSON S. GING AND JULIAN M. STURTEVANT[2]

RECEIVED DECEMBER 23, 1953

The hydrolysis of inorganic pyrophosphate, catalyzed by crystalline yeast pyrophosphatase, has been studied calorimetrically at 25°, in the presence of magnesium ions to activate the enzyme. The enthalpy change accompanying the reaction at *p*H 7.3 is -5810 ± 130 cal. per mole of pyrophosphate. This value is considered to be free from contributions resulting from a change in the ionization state of the buffer (veronal or orthophosphate) or the difference in the heat contents of magnesium pyro- and orthophosphates.

Introduction

In attempts to understand the mechanisms by which the free energy of respiration is converted into work, it is important to have available accurate thermodynamic, and in particular free energy, data for the individual reactions which may be involved. This has been the cause of the numerous estimates which have been made of the standard free energy of hydrolysis of the terminal phosphoric anhydride bond of adenosinetriphosphate (ATP). These estimates, which are necessarily arrived at by rather cumbersome routes, have ranged from $-12{,}000$ cal. per mole to $-9{,}000$ cal. per mole.[3]

Inorganic pyrophosphate also contains a phosphoric anhydride bond. The recent crystallization by Kunitz[4] of an enzyme which catalyzes the hydrolysis of pyrophosphate affords the opportunity[5] of determining the heat of the hydrolysis under reasonably well-defined conditions. This datum should be of interest in the eventual evaluation of the free energy of hydrolysis of the anhydride bond in pyrophosphate.

The heat of hydrolysis of pyrophosphoric acid in 71% sulfuric acid has been determined by Giran.[6] He found $\Delta H = -4{,}420$ cal. per mole for the reaction

$$H_4P_2O_7(aq) + H_2O = 2H_3PO_4(aq)$$

Recently Ohlmeyer and Shatas[7] have reported measurements of the heat of hydrolysis of inorganic pyrophosphate catalyzed by pyrophosphatase obtained from baker's yeast. They obtained the value $\Delta H = -8{,}950$ cal. per mole, in veronal buffer *p*H 7.2 at 29°.

Experimental Procedures

The calorimetric procedure employed has been described in detail.[8] All measurements were carried out at $25.00 \pm 0.05°$. *p*H measurements were made with a Beckman Model G meter and Type E glass electrode, taking the *p*H of a 0.025 *M* KH_2PO_4–0.025 *M* Na_2HPO_4 solution to be 6.86 at 25°.

Enzyme.—Crystalline inorganic pyrophosphatase was kindly supplied by Dr. M. Kunitz of the Rockefeller Institute for Medical Research. Stock solutions were prepared and kept frozen at −10° when not in use. As reported by Kunitz,[4] the enzyme is rather unstable at room temperature in very dilute solution. Since our calorimetric method requires a thermal equilibration period of 12 to 15 hr. at the reaction temperature, considerable loss of enzyme activity was experienced. In all the later experiments, for which rate constants are reported, the enzyme solution contained orthophosphate. This was found to have a pronounced effect in stabilizing the enzyme, as might be expected since orthophosphate is a substrate for the enzyme.

Substrate.—$Na_4P_2O_7 \cdot 10H_2O$ (Mallinckrodt Analytical Reagent) was recrystallized several times from warm water. After air drying at room temperature the water content determined by drying to constant weight at 105° was found to be $98.6 \pm 0.2\%$ of the theoretical value for the decahydrate. Colorimetric determination of orthophosphate indicated $0.6 \pm 0.3\%$ impurity calculated as $Na_3PO_4 \cdot 12H_2O$. Acid hydrolysis followed by colorimetric determination of the orthophosphate formed showed a pyrophosphate content of $99.2 \pm 0.3\%$ calculated as $Na_4P_2O_7 \cdot 10H_2O$. All data given below are based on the crystalline substrate as 100% $Na_4P_2O_7 \cdot 10H_2O$.

(1) This research was supported in part by a grant-in-aid from the National Science Foundation.

(2) To whom inquiries concerning this communication should be addressed.

(3) See the summary given by K. Burton and H. A. Krebs, *Biochem. J.*, **54**, 94 (1953).

(4) M. S. Kunitz, *J. Gen. Physiology*, **35**, 423 (1952).

(5) The authors are indebted to Dr. J. S. Fruton for suggesting this reaction for calorimetric study.

(6) H. Giran, *Compt. rend.*, **135**, 961 (1902).

(7) P. Ohlmeyer and R. Shatas, *Arch. Biochem. Biophys.*, **36**, 411 (1953).

(8) A. Buzzell and J. M. Sturtevant, THIS JOURNAL, **73**, 2454 (1951),

Determination of Orthophosphate.—The following procedure was found to avoid any hydrolysis of pyro- to orthophosphate,[4] and gave a color which was stable for at least 5 hr. To 5 ml. of 0.2 N H_2SO_4 is added a sample containing 0.08 mg. or less of orthophosphate phosphorus. After the addition of 5 ml. of a 5% ammonium molybdate solution and 1 ml. of a 1% solution of hydroquinone,[9] the mixture is allowed to stand at room temperature for 10 to 20 minutes. One ml. of a $NaHSO_3$–Na_2SO_3 solution (95 ml. of 15% $NaHSO_3$ plus 5 ml. of 20% Na_2SO_3) is added, the solution is diluted to 25 ml., and the optical density at 810 mμ is determined after 30 minutes or more.

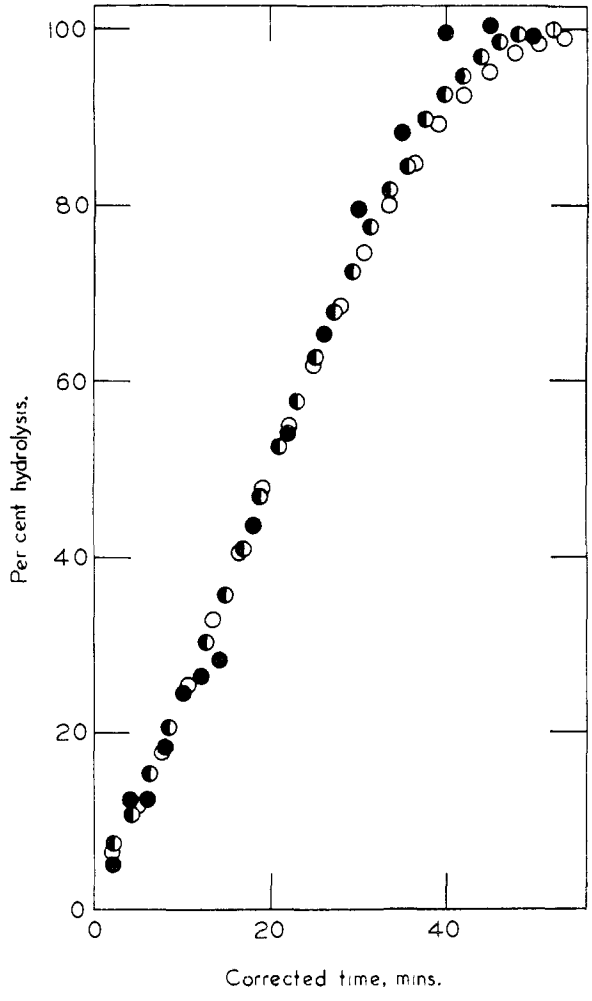


Fig. 1.—Comparison of analytically and calorimetrically determined kinetics: ●, analytical; ◐, calorimeter A; ○, calorimeter B. See text for correction of time.

Results

Experiments in Veronal Buffers.—Reactions were carried out in 0.05 M veronal buffers primarily to permit a comparison between the calorimetrically observed kinetics and the kinetics determined by analysis of the reaction mixture for orthophosphate. The data for these experiments are summarized in Table I.

The rates observed in these reactions are of no absolute significance because of loss of enzymatic activity during the thermal equilibration. The reactions were found to be zero order in the substrate to 75–80% completion. The total heat of reaction

(9) S. R. Benedict and R. C. Theis, *J. Biol. Chem.*, **61**, 63 (1924).

TABLE I

HYDROLYSIS OF INORGANIC PYROPHOSPHATE AT 25° IN VERONAL BUFFERS

Total buffer concn. = 0.05 M; ionic strength = 0.1 M,

Run	Initial pyrophosphate, concn., moles/l. × 10^4	Magnesium sulfate, concn., moles/l. × 10^4	Final pH	$-\Delta H$, cal. per mole
1	3.79	3.75	7.35	7410
2	3.79	3.75	7.35	7060
3	2.66	2.50	7.49	7250
4	2.66	2.50	7.51	7310
5	3.91	3.75	7.64	7550
6	3.91	3.75	7.64	7280
			Mean	7310 ± 180

was evaluated by extrapolating the linear portion of the $(r_\infty - r)$ *vs.* time curve back to the time of initiation of the reaction; r is the integrator[8] output reading at time t, corrected for the drift rate observed after the completion of the reaction, and r_∞ is evaluated by subtracting this drift from the readings obtained after the completion of the reaction.

The solutions used in runs 5 and 6 in Table I also were used in a kinetic experiment performed outside the calorimeters, in which the rate of hydrolysis was determined by periodic determination of orthophosphate in the reacting mixture. The calorimetric runs are compared with this analytical run in Fig. 1, in which the percentage completion is plotted against the time. In the calorimetric runs the percentage completion was taken equal to the quantity $100\ (r_\infty - r)/(r_\infty - r_0)$. Because of the gradual loss of enzymatic activity at room temperature (which was more rapid in the tantalum calorimeters than in glass), it has been necessary to change the time scale of the two calorimetric runs; in each case the observed times were multiplied by the factor (0.523 for calorimeter A, run 5, and 0.478 for calorimeter B, run 6) necessary to make the time of half-completion the same as observed in the analytical experiment. It is seen that the time course of the heat evolution agrees rather closely with that of the appearance of orthophosphate. A similar comparison, with similar results, was made between calorimetric runs 1 and 2 of Table I and an analytical run using the same solutions. We have therefore assumed that within experimental error the heat evolution observed is due only to the hydrolysis of pyrophosphate to orthophosphate, plus any accompanying process or processes proceeding with essentially the same over-all kinetics.

In the hydrolysis of pyrophosphate in unbuffered solution at pH 7.5 the pH decreases during the reaction. It was found that approximately 0.1 mole of alkali was required per mole of pyrophosphate hydrolyzed to restore the final pH to its initial value. The heat of ionization of the protonated form of veronal might be expected to be of the order of −10,000 cal. per mole, so that something like 1000 cal. per mole should be added to the heat of reaction observed in veronal buffer to correct[10] for the change in the ionization state of the buffer.

(10) A. Dobry and J. M. Sturtevant, *ibid.*, **195**, 141 (1953).

The resulting figure, approximately −6300 cal. per mole, is similar to the value observed in low concentrations of phosphate buffer (Table II).

The precision uncertainty interval[11] given for the mean ΔH in Table I includes the uncertainty in the calorimeter calibrations and an allowance of $\pm 1/2\%$ for the purity of the sodium pyrophosphate.

Experiments in Phosphate Buffers.—Most of our experiments were performed with solutions containing a rather large ratio of orthophosphate ions to pyrophosphate ions, in order to avoid the problem of including corrections for the heat of ionization of the buffer. The pyrophosphate ions present have the formulas $H_iP_2O_7$ with a charge of $(i - 4)$, where $i = 0, 1, 2, 3, 4$. Consider the species $HP_2O_7^{=}$; hydrolysis of this with no change of pH would proceed according to the equation

$$HP_2O_7^{=} + H_2O = HPO_4^{=} + H_2PO_4^{-} \qquad (1)$$

Suppose the actual pH were such that some of the $H_2PO_4^-$ ions tended to lose protons; if the total orthophosphate concentration were large compared to the initial pyrophosphate concentration, then it is evident that any protons lost would be taken up by $HPO_4^=$ ions supplied by the buffer. A similar argument holds for the other types of pyrophosphate ions. We thus see that if the orthophosphate concentration is sufficient to hold the pH substantially constant during the reaction, the observed reaction heat will not be complicated by any buffer ionization heat.

It would be desirable to obtain from the observed heats the heats for the hydrolysis of individual types of pyrophosphate ions. At pH 7 the major species present are $H_2P_2O_7^=$ and $HP_2O_7^{=}$. However, the pK values and heats of ionization available for pyrophosphoric acid are insufficiently reliable to make it possible to evaluate from the experimental data the heat of a reaction of the type represented by equation 1.

It is known[12] that magnesium phosphate and pyrophosphate are rather weak electrolytes. In order to secure good zero-order kinetics so that reliable extrapolations of the calorimetric heat *vs.* time curves could be made, it seemed advisable, in the light of the work of Kunitz,[4] to use concentrations of magnesium ions approximately equal to the initial pyrophosphate concentrations. There thus arises the possibility that there may be some heat effect associated with the fact that magnesium ions initially bound by pyrophosphate end up bound by orthophosphate. To investigate this point, and to demonstrate that the hydrolysis proceeds essentially to completion, reactions were run in orthophosphate buffers of concentrations up to 0.2 M.

The data for reactions carried out in phosphate buffers are summarized in Table II. Enzyme concentrations and rate constants are listed for those experiments in which the enzyme stock solutions contained phosphate as stabilizer. The concentrations of these solutions calculated from the optical density[4] at 280 mμ agreed well with that deduced from the weight of dry enzyme used. Ionic strengths were made up to the indicated values by addition of sodium chloride.

(11) F. D. Rossini and W. E. Deming, *J. Wash. Acad. Sci.*, **29**, 416 (1939).

(12) Tabor and Hastings, *J. Biol. Chem.*, **148**, 627 (1943); K. Burton and H. A. Krebs, *Biochem. J.*, **54**, 94 (1953); private communication from J. Berthet, University of Louvain.

TABLE II

HYDROLYSIS OF INORGANIC PYROPHOSPHATE AT 25° IN PHOSPHATE BUFFERS

Run	Initial concn., moles/l. Pyrophosphate, × 10^4	Magnesium sulfate, × 10^4	Orthophosphate	Ionic strength	Enzyme concn., γ/ml.	Final pH	k, specific reaction rate,[a] × 10^7	$-\Delta H$, cal. per mole
1	5.03	5.00	0	0.1	..	7.45	..	7670
2	5.03	5.00	0	.1	..	7.48	..	7340
3	3.00	3.02	1×10^{-5}	.6	1.45	6.98	0.64	6840
4	3.00	3.01	0.0050	.6	0.72	7.15	2.10	6200
5	3.33	2.26	.0075	.075	..	7.27	..	7050
6	3.33	2.26	.0075	.075	..	7.27	..	6870
7	3.02	2.25	.0075	.075	..	7.60	..	6280
8	3.02	2.25	.0075	.075	..	7.61	..	6190
9	3.00	3.00	.0099	.6	1.35	7.16	2.60	6040
10	2.61	2.52	.0101	.1	..	6.87	..	6380
11	2.61	2.52	.0101	.1	..	6.87	..	6970
12	2.61	2.54	.0102	.1	..	6.87	..	6290
13	2.61	2.54	.0102	.1	..	6.87	..	6200
14	2.00	2.08	.0100	.1	..	7.36	..	6840
15	2.76	2.54	.0102	.1	..	7.47	..	6600
16	2.76	2.54	.0102	.1	..	7.47	..	6580
17	2.85	2.55	.0103	.1	..	7.88	..	6680
18	3.00	3.01	.0200	.6	0.72	7.19	2.65	6650
19	3.00	3.03	.0250	.6	2.18	7.18	2.77	5920
20	3.00	3.04	.0500	.6	2.90	7.27	1.51	5910
21	3.00	3.03	.0750	.6	2.18	7.27	1.66	5800
22	3.00	3.02	.100	.6	1.45	7.27	1.36	6080
23	5.29	5.08	.140	1.0	1.75	7.22	2.10	5700
24	3.00	3.04	.150	.6	2.90	7.30	.76	5630
25	5.32	5.08	.160	1.0	1.75	7.22	1.65	5900
26	5.47	5.08	.180	1.0	1.75	7.28	1.33	5770
27	3.00	3.06	.200	.6	4.35	7.37	.59	5700
							Mean of runs 20–27	5810 ± 130

[a] Units of k are moles liter^{-1} sec.$^{-1}$ per γ of enzyme per ml.

Comparison of various sets of runs at constant phosphate concentration fails to show any significant variation of the heat of reaction with pH. For example, runs 10 through 17 of Table II, all carried out in 0.01 M phosphate buffer at 0.1 M ionic strength, have a mean value of ΔH of −6570 cal. per mole, with an average deviation from the mean of ±4.3%, and cover the pH range from 6.9 to 7.9. A similar lack of dependence of ΔH on pH is indicated by the data of Table I for veronal buffers. There also seems to be no appreciable effect of ionic strength in the range covered.

There is a definite trend of the heat data toward lower (absolute) values as the concentration of orthophosphate is increased. This is shown in Fig. 2, in which all values of ΔH at a given phosphate concentration have been averaged to avoid overcrowding of the figure. We interpret this effect to indicate that a significantly greater proportion of the Mg ions present becomes bound by orthophosphate ions at the expense of that bound by pyrophosphate ions as the phosphate concentration is increased, so that the contribution to the observed heat effect of reactions such as

$$MgH_2P_2O_7 + HPO_4^{=} \longrightarrow H_2P_2O_7^{=} + MgHPO_4 \qquad (2)$$

is decreased. The fact that the observed ΔH remains essentially constant in the range of phosphate concentrations from 0.05 to 0.20 M indicates further that the shift of Mg ions from pyro- to orthophosphate is completed.

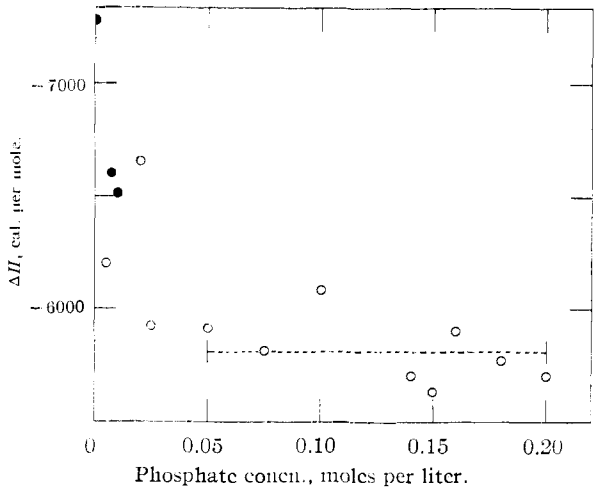


Fig. 2.—Variation of ΔH with orthophosphate concentration: ●, mean values; - - - -, mean of all runs from 0.05 M to 0.20 M.

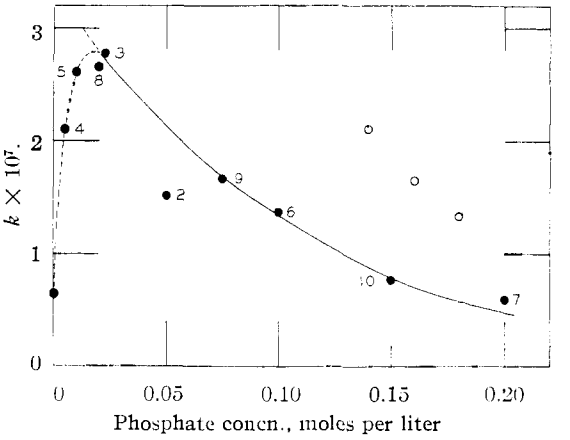


Fig. 3.—Variation of specific reaction rate (moles liter^{-1} sec.$^{-1}$ per γ of enzyme per ml.) with orthophosphate concentration: O, ionic strength 1.0 M, initial pyrophosphate concentration 5.3×10^{-4} M; ●, ionic strength 0.6 M initial pyrophosphate concentration 3.0×10^{-4} M. Numbers indicate chronological order of experiments.

It is evident that the observed change of ΔH with phosphate concentration cannot be due to incompleteness of the hydrolysis reaction. The forward rate in this reversible system is proportional to the first power of the pyrophosphate concentration while the reverse rate is proportional to the square of the orthophosphate concentration. Thus, under conditions of essentially constant initial pyrophosphate concentration, if the hydrolysis had been only 99% complete in 0.02 M phosphate no heat effect should have been observed in 0.2 M phosphate. Furthermore, it has been shown[13] that pyrophosphate is essentially completely hydrolyzed in 4 M phosphate, provided enough Mg^{++} is added to activate the enzyme.

On this basis we select for the heat of hydrolysis of pyrophosphate at pH 7.3 the mean of the values obtained between 0.05 and 0.2 M phosphate concentrations, $\Delta H = -5810 \pm 130$ cal. per mole. The precision uncertainty interval was estimated as outlined in connection with the data in Table I. This change in heat content, as explained above, contains no contribution due to change in the ionization state of the buffer, and is presumably also free from any complication due to a possible difference in the heat contents of pyro- and orthophosphates.

The rate data are plotted in Fig. 3 as a function of the phosphate concentration. The values at 0.6 M ionic strength are numbered in chronological order; it is evident that there was no appreciable loss in activity of the enzyme stock solution during this series of runs, which extended over a period of 3 weeks. Kunitz[4] has observed that the rate of hydrolysis increases with increasing initial pyrophosphate concentration; this, together with the difference in ionic strength, probably accounts for the larger rates at 1 M ionic strength.

According to the data of Kunitz[4] it is unlikely that more than a small fraction of the observed variation of rate can be attributed to variation of pH. The decrease of rate at low concentration is probably to be assigned to inactivation of the enzyme during thermal equilibration in the tantalum calorimeters, which is apparently prevented by higher phosphate concentrations.

The decrease in rate in the presence of high concentrations of phosphate may be due to either or both of two causes, product inhibition, or change of concentration of either an enzyme–activator complex or a substrate–activator complex.

Product inhibition would give rates varying according to an equation[14] of the form

$$1/k = A + B(PO_4)^2 \qquad (3)$$

in a case such as the present one where the reverse reaction is not detectable. In this equation, k is the rate constant in moles liter^{-1} sec.$^{-1}$ per unit enzyme concentration, A and B are constants, and (PO_4) represents the total phosphate concentration. The observed rates follow an equation of the expected form at concentrations above 0.01 M, with an average deviation, due in large part to the result at 0.05 M, of $\pm 10\%$ of the observed rate. However, more extensive data would be necessary to establish this as a case of product inhibition.

Kunitz[4] has shown that the rate of hydrolysis at constant initial pyrophosphate concentration depends on the concentration of Mg^{++}. This suggests that the decrease in rate at high phosphate concentrations might be due to a depletion of the concentration of Mg^{++} available for activating the enzyme. In the absence of more detailed data, of sufficient breadth to enable distinction between various alternative models for the activating influence of magnesium, it is not profitable to pursue further this possibility. It may be remarked here that it is difficult to understand the fact that accurately zero order kinetics is observed in pyrophosphate hydrolyses under a variety of conditions, in spite of the dependence[4] of hydrolysis rates on Mg^{++} concentration, pyrophosphate concentra-

(13) J. Berthet, P. Thibaut and L. Berthet, *Arch. intern. physiol.*, **61**, 245 (1953).

(14) J. M. Sturtevant, remarks at a symposium on the mechanism of enzyme action, McCollum-Pratt Institute, Johns Hopkins University, Baltimore, June, 1953 (in press).

tion, and other experimental conditions which change during a single experiment.

Discussion of Results

The heat of hydrolysis of pyrophosphate in dilute aqueous solution, catalyzed by non-crystalline enzymes, was reported by Ohlmeyer and Shatas[7] to be $\Delta H = -8950$ (average deviation $= \pm 440$) cal. per mole. Their solutions contained initially 2×10^{-3} M pyrophosphate, 2×10^{-3} M orthophosphate and 2.5×10^{-4} M $MgCl_2$, and were buffered at pH 7.2 by 0.024 M veronal. Their measurements were carried out at 29°. The value for ΔH which we obtained in veronal buffer (Table I) is -7310 cal. per mole, 18% lower. The cause of this discrepancy is unknown.

A considerably more negative value for ΔH than -5810 cal. per mole is expected for the hydrolysis of a high energy phosphate bond. It is interesting to note that Berthet, Thibaut and Berthet[13] have obtained preliminary results indicating an unexpectedly small apparent equilibrium constant for this reaction.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

A New Series of Silicon Oxychlorides[1]

BY WALTER C. SCHUMB AND ROBERT A. LEFEVER[2]

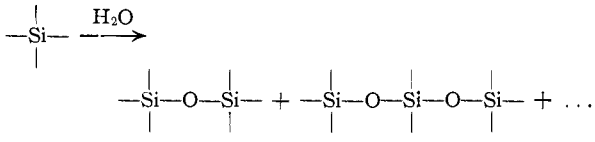
RECEIVED NOVEMBER 17, 1953

The partial hydrolysis of hexachlorodisilane, Si_2Cl_6, at −78° was found to result in a new series of silicon oxychlorides, represented by the general formula, $Si_{2n+2}O_nCl_{4n+6}$. The distinguishing feature of these compounds is the presence of alternating Si–Si and Si–O–Si linkages as the basic structure of the molecule. The first three members of the series, Si_4OCl_{10} (b.p. 130–131° (15 mm.)), $Si_6O_2Cl_{14}$ (b.p. 159–162° (3 mm.)), and $Si_8O_3Cl_{18}$ (b.p. 170–173° (2 mm.)), have been isolated and identified.

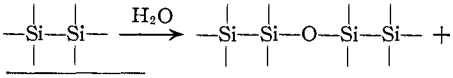
Introduction

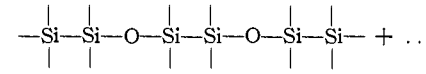
Although it had been known for some time that the direct chlorination of silicon and calcium silicide produced higher chlorides of the series Si_nCl_{2n+2}, it was not until 1941[3] that the existence of an analogous series, $Si_nO_{n-1}Cl_{2n+2}$, of silicon oxychlorides was clearly established by Schumb and Holloway. The oxychlorides were prepared in this work by the action of a mixture of oxygen and chlorine on silicon at red heat. The absence of appreciable quantities of higher chlorides of silicon in the products was noted indicating that the silicon–silicon bonds were effectively ruptured in the process.

In 1950, Schumb and Stevens[4] reported the preparation of oxychlorides of the series $Si_nO_{n-1}Cl_{2n+2}$, by the partial hydrolysis of silicon tetrachloride at −78°. The success of this method suggested to us a possible means of preparing oxychlorides containing alternating Si–Si and Si–O–Si linkages in the same molecule. Thus, in a reaction analogous to the partial hydrolysis of silicon tetrachloride (bonds without second atoms refer to chlorine bonds), the partial hydrolysis of hexa-



chlorodisilane might be expected to result in a new series of oxychlorides by the reaction





Although rupture of Si–Si bonds could yield oxychlorides of the established series (actually, evidence for the occurrence of such a side reaction during hydrolysis was not found), higher chlorides would not be expected, thus simplifying the problem of separation.

In a preliminary communication,[5] isolation of the first member, Si_4OCl_{10}, of the new series, $Si_{2n+2}O_nCl_{4n+6}$, was reported. In the following work, further evidence for the existence of this compound as well as the second, $Si_6O_2Cl_{14}$, and third, $Si_8O_3Cl_{18}$, members of the new series is presented.

Experimental

Procedure.—Hexachlorodisilane was diluted with anhydrous diethyl ether, cooled to −78° in a solid carbon dioxide–trichloroethylene bath and hydrolyzed by the gradual addition of a measured quantity of water. The hexachlorodisilane used in this work was prepared by the chlorination of calcium silicide as described in reference 6. Analytical reagent ether was redistilled and stored over sodium.

The reactions were carried out in a 1-liter, three-necked round-bottom flask fitted with a mercury-seal stirrer. One neck of the flask was connected directly to a water condenser to allow removal of ether after the reaction, while the other neck was used for the introduction of reagents. The hexachlorodisilane was added to the ether in the flask and the mixture was cooled, with stirring, to −78°. The desired quantity of water was then added dropwise from a 10-ml. buret. After the addition of water, the contents of the flask was held at −78°, with constant stirring, for about two hours and then allowed to warm to room temperature. The amounts of ether, hexachlorodisilane and water were varied in order to obtain information concerning the optimum molar ratios for oxychloride formation.

After removal of the ether by distillation directly from the reaction flask, the remaining material was transferred to a fractionation column. The unreacted hexachlorodisilane (b.p. 45° (15 mm.)) was recovered by fractionation under

(1) Based on part of a thesis presented by R. A. Lefever to the Department of Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Owens-Illinois Research Fellow, 1952–1953.

(3) W. C. Schumb and D. F. Holloway, THIS JOURNAL, **63**, 2753 (1941).

(4) W. C. Schumb and A. J. Stevens, *ibid.*, **72**, 3178 (1950).

(5) W. C. Schumb and R. A. Lefever, *ibid.*, **75**, 1513 (1953).

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