[CONTRIBUTION FROM THE MONSANTO CHEMICAL CO. RESEARCH DEPARTMENT, PHOSPHATE DIVISION]

Structure and Properties of the Condensed Phosphates. VII. Hydrolytic Degradation of Pyro- and Tripolyphosphate

BY J. R. VAN WAZER, E. J. GRIFFITH AND J. F. MCCULLOUGH

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The rates of hydrolysis of 1% solutions of tetramethylammonium tripoly- and pyrophosphates were measured at 30, 60, 90 and 125°, at constant *p*H values of 1, 4, 7, 10 and 13 in the presence of tetramethylammonium bromide. Tripolyphosphate was also studied in the absence of the electrolyte. In addition sodium tripolyphosphate was hydrolyzed both in the absence and the presence of 0.65 *N* sodium bromide at several values of *p*H and temperature. The hydrolyses follow a first-order law and are catalyzed by acid and not by base Formation of polyphosphato–sodium complexes also increases the rate. The activation energy for the process ranges from 20 to 40 kcal. under various conditions. For non-complexing cations (tetramethylammonium), it increases as the *p*H is raised.

Introduction

More than fifty papers have been published during the last one hundred years concerning the hydrolytic degradation of condensed phosphates. The inadequacies of the published data, combined with the growing demand for hydrolysis information, necessitated this extensive study of the variables known to influence hydrolysis. The data presented herein will be of prime value in interpreting the "high energy bond"[1] of the biochemists and in affording quantitative information to persons engaged in the industrial applications of the phosphates.

It has long been known[2] that condensed phosphates react with water to form less condensed phosphates and ultimately orthophosphates. It is well established that the hydrolysis of pyrophosphate is governed by pseudo-first-order kinetics,[3,4] and data are available to show that the activation energy is about 25 kcal.[4,5] The effect of *p*H has been studied,[5,6] and, in addition, it has been shown that an atmosphere of neutral salt[5,6] influences the reaction. Cations that are strongly complexed by condensed phosphates also enter into the reaction, but little is known concerning their action.[7] Other variables that have been studied are catalysis by enzymes[8] and by precipitated metal oxides.[9] These catalysts have an enormous accelerating action on the rates of degradation of condensed phosphates; and more information is available about their action than there is about the uncatalyzed hydrolysis process.

Experimental

The thermostats employed were set at 30, 60 and 90°, with water being used as the heat-transfer medium. The 30° bath was capable of maintaining a constant temperature of about ±0.01°, while the 90° bath was capable of no better than ±0.1°. A pressure cooker was used to reach the 125° temperatures. It was heated with a Lindberg hot-plate. Usually five minutes was needed to raise the temperature from 100° to the final value of 125°. The latter temperature was maintained within ±0.2° throughout the remainder of most runs.

Containers.—Four-liter, soft glass, wide-mouthed bottles were used to contain the samples below *p*H 10. The wide mouth was required to accommodate the immersion of glass and calomel electrodes that were used in checking the *p*H of the samples. At *p*H values of 10 and 13, considerable trouble was experienced in obtaining containers that would not be attacked by tetramethylammonium hydroxide at high temperatures. Alkali-resistant glasses[10] were first tried, but unsuccessfully. Secondly, an attempt was made to use polyethylene liners, but these were too weak to withstand the temperature and small hydrostatic pressure imposed upon them. The next attempt was made with polyethylene bottles. These were satisfactory at 60°, but at 90° the alkali and heat caused the polyethylene to polymerize to a brittle state so that the bottles cracked. The problem was solved by machining a bottle from a fluorocarbon block (Teflon).

Titrometer and *p*H Meters.—The solutions were analyzed by means of the Precision-Dow recording titrometer.[11] This instrument was particularly useful in this work because interferences such as carbonate could be readily detected, and a record of each pertinent analysis was obtained for further study.

A Beckman *p*H meter was used to adjust the *p*H of samples for hydrolysis. For low values of *p*H, the meter was standardized against a *p*H 4 buffer, and for values of *p*H near neutrality, a *p*H 7 buffer was employed. For high values of *p*H, the *p*H 10 buffer was used, and a sodium ion correction[12] was applied for systems containing sodium ions. All standardizations were carried out at the temperature of the solution being measured.

Chemicals.—Sodium triphosphate hexahydrate was used as a source of triphosphate-ions. It was prepared by repeated precipitation of Monsanto triphosphate from aqueous solution with methyl alcohol. All samples analyzed to be better than 99.5% sodium triphosphate hexahydrate and exhibited the proper Na_2O/P_2O_5 ratio to within the precision of the analysis (±0.1%). Analytical reagent grade tetrasodium pyrophosphate decahydrate, obtained from Mallinckrodt Chemical Works, was used as a source of pyrophosphate anions.

Tetramethylammonium bromide was purchased from Eastman Kodak. Tetramethylammonium hydroxide was prepared by treating tetramethylammonium bromide with carbonate-free silver oxide, which had been made from C.P. silver nitrate and carbonate-free sodium hydroxide. All reactions in this preparation were performed in an atmosphere of nitrogen. Tetramethylammonium polyphosphates were prepared by ion-exchanging sodium phosphates with a hydrogen form of finely divided (200–400 mesh) Dow-X-50 cation-exchange resin, and neutralizing the resulting polyphosphoric acid with tetramethylammonium hydroxide. These exchanges were done batchwise. About twenty g.

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(1) See, for example, F. Lipman, *Advances in Enzymol.*, **1**, 99 (1941); also O. Meyerhof, *Ann. N. Y. Acad. Sci.*, **75**, 377 (1944).

(2) A. Reynoso, *Ann.*, **83**, 98 (1852); *Compt. rend.*, **34**, 795 (1852).

(3) H. Giran, *Ann. chim. phys.*, [VII], **30**, 203 (1903).

(4) G. A. Abbott, THIS JOURNAL, **31**, 763 (1909); S. J. Kiehl and E. Claussen, *ibid.*, **55**, 2284 (1935).

(5) D. O. Campbell and M. L. Kilpatrick, *ibid.*, **76**, 893 (1954).

(6) P. Sabatier, *Compt. rend.*, **106**, 63 (1888); *ibid.*, **108**, 738 (1890); *Bull. soc. chim.*, **1**, 702 (1889); M. Berthelot and G. Andre, *Compt. rend.*, **123**, 776 (1896); *ibid.*, **124**, 265 (1897); especially R. Watzel, *Die Chemie*, **55**, 356 (1942); also J. Muus, *Z. physik. Chem.*, **159A**, 268 (1932); A. Kailan, *ibid.*, **160A**, 301 (1932).

(7) J. Green, *Ind. Eng. Chem.*, **42**, 1542 (1950).

(8) J. Roche, "Phosphatases" in "The Enzymes, Chemistry and Mechanism of Action," Vol. 1, Part 1 (Ed. by Sumner and Myrback), Academic Press, Inc., New York, N. Y., 1950, pp. 473–510.

(9) E. Bamann and M. Meisenheimer, *Ber.*, **71B**, 2086 (1938); *ibid.*, **71B**, 2233 (1938); E. Bamann, *Angew. Chem.*, **52**, 186 (1939); *Naturwissenschaften*, **28**, 142 (1940), and E. Bamann and Heumuller, *ibid.*, **28**, 535 (1940).

(10) *E.g.*, Corning Alkali Resistant Glass No. 728.

(11) H. A. Robinson, *Trans. Electrchem. Soc.*, **92**, 445 (1947).

(12) Bulletin 225A, Beckman Instruments, Inc., South Pasadena, California.

of damp resin was slurried per g. of phosphate, and the mixture was stirred for three minutes and then filtered. All other chemicals were standard laboratory reagents and were C.P. grade.

Preparation of Solutions for Hydrolysis.—The preparation of solutions for hydrolysis varied slightly, depending upon the conditions under which the phosphates were to be hydrolyzed. The steps which were followed during the preparation of a sample of tetramethylammonium phosphate in 0.65 *N* tetramethylammonium bromide solution were as follows: Enough phosphate was weighed out to yield a 1% final solution of orthophosphoric acid on complete hydrolysis and ten per cent. excess was added for the loss in ion-exchange resin. This phosphate was dissolved in *ca.* 500 ml. of water, and *ca.* 1000 g. of the hydrogen form of the ion-exchange resin was slurried into the resulting solution. After stirring three minutes, the resin was removed by suction filtration, and the filtrate was diluted to 950 ml. with water about 5° hotter than the required temperature. This solution was then added to 1000 ml. of 1.30 *N* tetramethylammonium bromide solution which was at temperature in the thermostated hydrolysis vessel. The *p*H was adjusted within ±0.1 *p*H unit of the required value by adding close to 50 ml. of relatively concentrated, carbonate-free tetramethylammonium hydroxide or hydrobromic acid, using a magnetic stirrer. The solution was then placed in the constant temperature bath. From three to five minutes was required between the time the phosphate was removed from the filter flask and the time it was placed in the bath. Zero time was arbitrarily set as the time the phosphate was mixed with the tetramethylammonium bromide solution. Periodically, the *p*H values of the solutions were measured; and, if they were in need of adjustment, enough tetramethylammonium hydroxide was added to bring them back to the proper *p*H.

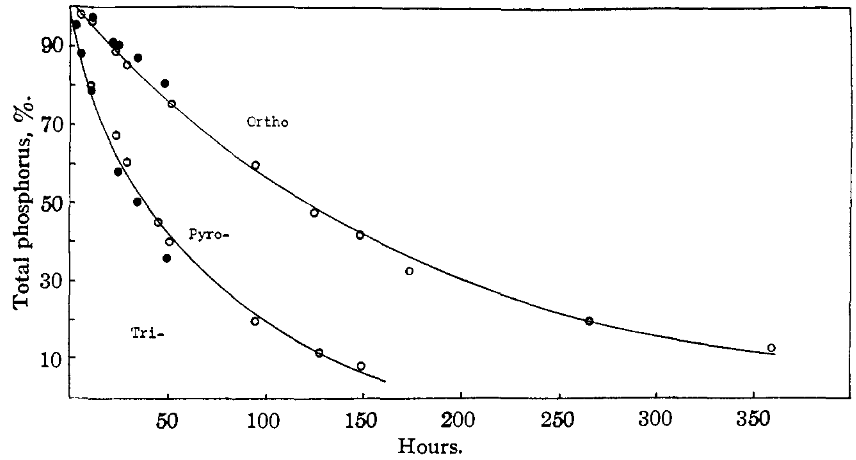

Fig. 1.—The hydrolysis of tetramethylammonium triphosphate in 0.65 *N* tetramethylammonium bromide solution at *p*H 4 and 60°: O, initial hydrolysis; ●, repeat hydrolysis.

The tetramethylammonium phosphate systems without added tetramethylammonium bromide were prepared by essentially the same procedure as above. The solutions containing sodium salts were made in a slightly different manner. In this case, a solution of 0.65 *N* sodium bromide was placed in the thermostat, and the solid sodium phosphate to be hydrolyzed was added directly to the solution with stirring but without ion exchange. The *p*H of these solutions was adjusted and maintained with either hydrobromic acid or sodium hydroxide, depending on which was needed. Based on previous work,[13] the assumption has been made throughout this study that the species of added anion in the neutral salt makes little or no difference to the hydrolysis as long as the charge per anion is unity.

Analysis.—*p*H titrations were used to analyze the solutions in this work.[14] Orthophosphate analyses were performed by a modified method of Gerber and Miles.[15] In all cases, the automatic titrometer[11] was employed.

Twenty-five ml. of phosphate solution was added to 75 ml. of water for analysis. The solution was adjusted to about *p*H 3 and then titrated past *p*H 10. A break occurs in the titration curve at a *p*H near 4.5 and a second break near *p*H 9.5. The exact *p*H values of these breaks depend upon the system being studied. This titration was a measure of the weak acid function of the system.

At the completion of the above titration, the phosphate solution was acidified until *p*H 3 was again obtained, and the titration was started just as before. In this case, the titration was stopped after the *p*H 4.5 end-point. Fifty ml. of 1 *N* silver nitrate was added at this point, and the titration continued until a strong acid end-point was obtained. The difference between the silver titration and the weak acid titration is equivalent to the orthophosphate of the system. In the case of pyrophosphate these two titrations are sufficient to define the system, but *p*H titration after complete hydrolysis (by boiling in strong acid) is additionally required for the triphosphate determination. The following equations were used in interpreting the triphosphate analyses

$$T = S - W \tag{1}$$

$$P = \frac{3W - 2S - O}{2} \tag{2}$$

where S is the number of equivalents of strong acid function in a sample; T is the number of moles of triphosphate; P is the number of moles of pyrophosphate; O is the number of moles of orthophosphate; W is the number of equivalents of weak acid function. The equation used in the analysis of the pyrophosphate solution is

$$P = (W - O)/2 \tag{3}$$

where the symbols have the same meanings as above. In each instance the orthophosphate concentration, O, was determined by the Gerber–Miles-type titration.

It should be noted that all hydrolyses, except some done at 125°, were carried through two or more half-lives. This means that about 2 yr. was needed to measure rate constants of 1×10^{-4} hr.$^{-1}$ and 12 min. for a 5 hr.$^{-1}$ rate constant.

Results and Discussion[16]

The measured specific rate constants for the disappearance of pyro- and triphosphate are presented in Table I as a function of temperature and *p*H. The hydrolyses on which these constants were based all followed the first-order rate law, as was shown by plotting the analytical data. It should be noted that the first-order rate constant fitted to the data obtained on a 4% solution of tetramethylammonium triphosphate with swamping electrolyte at *p*H 4 and 60° was 1.04 times greater than that for a 1% concentration under the same conditions. From the consideration of all experiments, it appears that this 1.04 factor is wholly attributable to experimental error.

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[13] J. R. Van Wazer and D. A. Campanella, This Journal, **72**, 655 (1950).

[14] J. R. Van Wazer, E. J. Griffith and J. F. McCullough, *Anal. Chem.*, in press.

[15] A. B. Gerber and F. T. Miles, *Ind. Eng. Chem., Anal. Ed.*, **13**, 406 (1941).

[16] Material supplementary to this article has been deposited as Document number 4341 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $13.75 for photoprints, or $4.50 for 35 mm. microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

TABLE I

OBSERVED FIRST-ORDER RATE CONSTANTS FOR DISAPPEARANCE OF THE ORIGINAL MOLECULE-ION

Phosphates being hydrolyzed	Swamping electrolyte	*p*H	Rate constant in hr.$^{-1}$ at 30°	60°	90°	125°
1% tetramethylammonium pyro-	0.65 *N* tetramethylammonium bromide	1	1.29×10^{-3}	4.05×10^{-2}	7.00×10^{-1}	
		4	1.08×10^{-4}	6.42×10^{-3}	1.89×10^{-1}	
		7		9.97×10^{-4}	4.12×10^{-2}	
		10			6.72×10^{-4}	(8×10^{-2})
		13				(5×10^{-3})
1% sodium pyro-	0.65 *N* sodium bromide	1		3.45×10^{-2}		
		4		9.04×10^{-3}		
1% sodium pyro-	No added electrolyte	1		6.39×10^{-2}		
		4		7.38×10^{-3}		
1% sodium pyro-	0.65 *N* sodium chloride	4		8.50×10^{-3}		
1% tetramethylammonium tri-	0.65 *N* tetramethylammonium bromide	1	1.12×10^{-2}	4.12×10^{-1}	5.41	
		4	3.99×10^{-4}	1.77×10^{-2}	3.74×10^{-1}	
		7	9.81×10^{-5}	2.80×10^{-3}	1.08×10^{-1}	
		10		2.85×10^{-4}	1.58×10^{-2}	(4×10^{-1})
		13			3.05×10^{-3}	(2×10^{-1})
4% tetramethylammonium tri-	0.65 *N* tetramethylammonium bromide	4		1.84×10^{-2}		
1% tetramethylammonium tri-	1.30 *N* tetramethylammonium bromide	4		1.26×10^{-2}		
1% tetramethylammonium tri-	No added electrolyte	1	3.27×10^{-2}			
		4		2.33×10^{-2}	4.62×10^{-1}	
		7		3.62×10^{-3}	1.47×10^{-1}	
		10		3.17×10^{-4}	1.72×10^{-2}	
		13			3.26×10^{-3}	
1% sodium tri-	0.65 *N* sodium bromide	4		3.65×10^{-2}	8.57×10^{-1}	
		7		5.62×10^{-3}	1.92×10^{-1}	
		10		1.93×10^{-3}	5.00×10^{-2}	(6)
		13			3.30×10^{-2}	
1% sodium tri-	No added electrolyte	4		2.39×10^{-2}	7.66×10^{-1}	
		7		4.51×10^{-3}	1.52×10^{-1}	
		10		1.23×10^{-3}	2.14×10^{-2}	

In the case of the hydrolysis of the triphosphate molecule-ion, plots of the analytical data showed the build-up of pyro- as well as of orthophosphate. Figure 1 shows the relative percentage of the total phosphorus present as tri-, pyro-, and orthophosphates throughout an hydrolysis experiment. Rate constants calculated for pyrophosphate hydrolyses from the triphosphate data were always in good accord with those measured directly on the pyrophosphate itself. However, the constants calculated in this way were usually not as reproducible (and hence accurate) as the ones measured directly.

Table II compares the quantity of pyrophosphate found by analysis during the hydrolysis of triphosphate in 0.65 *N* tetramethylammonium bromide solution at *p*H 4 and 60° to the quantity of pyrophosphate calculated from the equation

$$C_P = C_{T_0} \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

where

C_P = concn. of pyrophosphate at time, t
C_{T_0} = initial concn. of triphosphate
k_1 = specific rate constant for triphosphate in 0.65 *N* tetramethylammonium bromide at *p*H 4 and 60°
k_2 = specific rate constant for pyrophosphate in 0.65 *N* tetramethylammonium bromide soln. at *p*H 4 and 60° obtained from the hydrolysis of pyrophosphate

Crowther and Westman[17] also find that tri- and pyrophosphate hydrolyze independently of each other when they are mixed. The rate constants reported in Table I are based on replicate determinations. Figure 2 shows a typical plot of the log

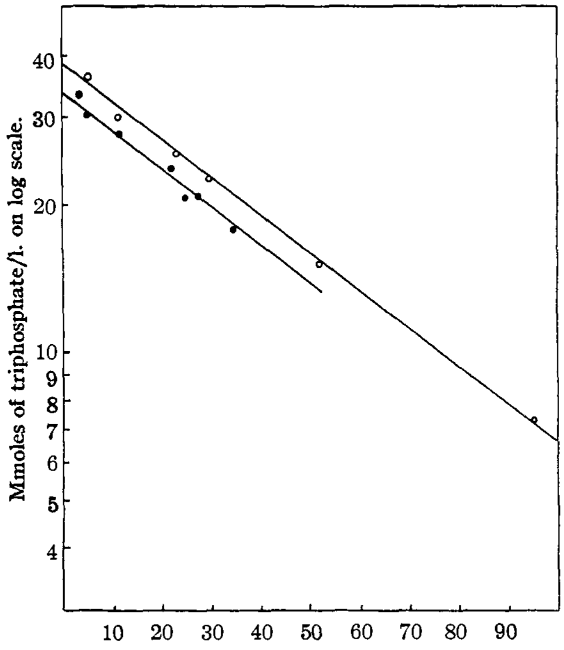

Fig. 2.—The hydrolysis of tetramethylammonium triphosphate in 0.65 *N* tetramethylammonium bromide solution at *p*H 4 and 60°: O, initial hydrolysis; ●, repeat hydrolysis.

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[17] J. P. Crowther and A. E. R. Westman, *Can. J. Chem.*, **32**, 42 (1954).

of triphosphate concentration *versus* time. From comparison of the replicates, it was estimated that the experimental error was about 5% for rate constants in the range of 10^{-1} to 10^{-3} hr.$^{-1}$ and increased to 10% for rate constants near 10^{-4} hr.$^{-1}$ All measurements at 125° were subject to additional errors, the total error for such measurements being about 75% or less.

The activation energy, E, which measures the temperature dependence, and the entropy of activation, $\Delta S^{\ddagger}$, which gives the gain in entropy on going from the original molecule-ion to the activated complex are presented in Table III. In addition, the free energy of activation, $\Delta F^{\ddagger}_{30°}$, computed for a temperature of 30° is given. These quantities are related to the rate constant at any temperature but at a fixed pH and ionic environment as[18]

$$k = \frac{\kappa T}{h} e^{-\Delta F^{\ddagger}/RT} = e\frac{\kappa T}{h} e^{\Delta S^{\ddagger}/R} e^{-E/RT}$$

where κ is the Boltzmann constant, h is Planck's constant, and T is the absolute temperature.

TABLE II

Time, hr.	Moles of pyrophosphate/l. calcd. as a consecutive first-order reaction product of triphosphate	Moles of pyrophosphate/l. found by analysis
11.13	10.1	9.7
22.83	11.3	11.6
29.25	14.2	14.0
51.88	19.5	19.7
95.00	22.7	22.4
125.08	20.1	19.3
148.75	18.4	19.4

TABLE III

ACTIVATION ENERGIES AND ENTROPIES AND FREE ENERGIES OF ACTIVATION FOR THE HYDROLYTIC DEGRADATION PROCESS

Salt being hydrolyzed	Swamping electrolyte	Parameter	Value of parameter at pH 1	pH 4	pH 7	pH 10	pH 13
1% tetramethylammonium pyrophosphate	0.65 N tetramethylammonium bromide	E	22.7 kcal.	27.2	29.8	(39.8)	
		$\Delta S^{\ddagger}$	−15 e.u.	−5	−1	(+18)	
		$\Delta F^{\ddagger}_{30°}$	27 kcal.	28	30	(34)	
1% tetramethylammonium triphosphate	0.65 N tetramethylammonium bromide	E	22.9 kcal.	24.8	26.0	30.3	(32.6)
		$\Delta S^{\ddagger}$	−10 e.u.	−11	−9	−2	(+1)
		$\Delta F^{\ddagger}_{30°}$	25 kcal.	27	28	30	(32)
1% tetramethylammonium triphosphate	No added electrolyte	E	....	23.8	29.4	31.7	....
		$\Delta S^{\ddagger}$	....	−13	0	+2	....
		$\Delta F^{\ddagger}_{30°}$	....	27	29	30	....
1% sodium triphosphate	0.65 N sodium bromide	E	....	25.1	28.1	25.8	....
		$\Delta S^{\ddagger}$	....	−8	−3	−12	....
		$\Delta F^{\ddagger}_{30°}$	....	27	28	30	....
1% sodium triphosphate	No added electrolyte	E	....	27.6	28.0	22.8	....
		$\Delta S^{\ddagger}$	....	−2	−4	−22	....
		$\Delta F^{\ddagger}_{30°}$	....	27	29	29+	....

Even though the concept of a simple activated complex may become untenable in view of presently undeveloped information which might indicate, say, an involved chain process, the activation entropy term still remains a convenient logarithmic notation for the frequency factors.

In Table I it should be noted that the rate constants for the hydrolysis of tetramethylammonium triphosphate with swamping electrolyte are more than twofold larger than those for the pyrophosphate under the same conditions. In neutral and somewhat acidic solutions, the triphosphate hydrolyzes somewhat less than three times faster than the pyrophosphate. At pH 1, the triphosphate goes about nine times faster than the pyro; and, in alkaline media, the triphosphate hydrolyzes 20 to 100 times faster. This is shown by the data of Table I and is supported by the build-up of pyrophosphate, which was measured during the triphosphate hydrolyses under various conditions. It is also in accord with the literature.[19] If the P–O–P linkages of pyro- and triphosphate were identical in reactivity, the equivalent rate constants for triphosphate should be twice that of pyro, since the triphosphate has twice as many rupturable linkages as has the pyrophosphate ion. Presumably, the excessively slow rate for the pyrophosphate degradation is attributable to the fact that its molecule-ions are symmetrical both in charge and atomic position in strongly basic or acidic solution. However, the $[O_3POPO_2(OH)]^{\equiv}$ ion, which appears in the neutral region, is unsymmetrical, and the P–O–P linkage in this molecule-ion is under more of the same influences as the P–O–P linkage in a triphosphate ion, partly because of the approximately equal electronegativities of hydrogen and phosphorus. This hypothesis is in accord with the fact that the entropy of activation for tetramethylammonium pyrophosphate with swamping electrolyte at pH 7 is about equal to that for tetramethylammonium triphosphate at pH 10–13. It should be noted in Table III that the $\Delta F^{\ddagger}_{30°}$ term, which is a direct measure of the over-all rate at 30°, is consistently about 2 kcal. higher for the pyro- than for the triphosphate, regardless of pH.

As shown in Table I, the rate of hydrolysis of tetramethylammonium triphosphate without swamping electrolyte is higher than that with swamping electrolyte, especially in acidic solutions. Thus, the ratio of the rate without swamping electrolyte to that with is 2.9 at pH 1, 1.3 at pH 4–7, and 1.1 at

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(18) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," 1st Ed., McGraw-Hill Book Co., New York, N. Y., 1941, pp. 195–199.

(19) S. L. Friess, THIS JOURNAL, **74**, 4027 (1952); also see Watzel of ref. 6.

*p*H 10–13. According to the Brönsted–Bjerrum rule,[20] this indicates a reaction between negative and positive ions in acidic solution and leads to the conclusion that the rate is catalyzed by hydrogen (hydronium) ion. Apparently at low values of the *p*H, the P–O–P linkage reacts with a $(H_3O)^+$ ion; but, as the *p*H is raised, this reaction plays a less important role with the reaction with neutral H_2O or hydrated cations becoming predominate at high *p*H.

At *p*H values of 4 and above, the case with sodium ion is just the reverse, as can be seen in Table I. When sodium was substituted for tetramethylammonium as the cation for either the pyro- or triphosphate at *p*H 4 and above, the ratio of the rate without swamping electrolyte to that with becomes a fraction (0.7 to 0.8), the value of which does not appear to depend on *p*H. Also, either with or without the presence of swamping electrolyte, the substitution of sodium for tetramethylammonium ion at *p*H 4 and above causes an increase in degradation rate—an effect which is more noticeable in the presence of the swamping electrolyte. As was pointed out in the communication[21] which preceded this paper, these effects must be considered as additional evidence for the formation of polyphosphato-sodium complexes, which have been shown to exist by other experiments.[13] The reports in the literature (*e.g.*, Watzel[6]) that there is a minimum rate of hydrolysis at *p*H 10, with an acceleration as the alkalinity is increased, do not show that the degradation is catalyzed by hydroxyl ion. Rather, the observed increase in rate on going to very strongly alkaline solutions is attributable to the sodium ion being added as NaOH.

In highly acidic solutions, the hydrogen ion seems to displace the sodium ion as a catalyst, so that addition of a sodium salt as swamping electrolyte results in a diminution in reaction rate in opposition to its accelerating action under less acidic conditions. This is borne out by the data in Table I for sodium pyrophosphate at *p*H 1 and 60°. The work by Friess[19] and by Campbell and Kilpatrick[5] describes this effect in more detail; but these authors do not show the accelerating action of sodium salts in mildly acidic, neutral and basic solutions, since the pertinent part of their work was done under conditions (strong acid) where the hydrogen ion was dominant.

Although we did not experimentally find its exact value, there must be a *p*H, perhaps varying with concentration, at which the addition of a sodium salt to a sodium pyro- or triphosphate solution has no effect on the rate of degradation of the phosphate. At this *p*H, the catalysis attributed to complex formation would be exactly balanced by the shielding effect of the type due to non-catalytic swamping electrolytes.

Our data for sodium pyrophosphate at *p*H 4 and 60° indicate that there is little difference between the effect of sodium bromide and sodium chloride swamping electrolytes. This agrees with the data of Campbell and Kilpatrick[5] and indicates that these anions are not involved in the hydrolysis process except indirectly by affecting activities.

DAYTON, OHIO

(20) J. N. Brönsted, *Z. physik. Chem.*, **102**, 109 (1922); *ibid.*, **115**, 337 (1925); and N. Bjerrum, *ibid.*, **108**, 82 (1924).

(21) J. R. Van Wazer, E. J. Griffith and J. F. McCullough, THIS JOURNAL, **74**, 4977 (1952).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CATHOLIC UNIVERSITY OF AMERICA]

The Hydrazino Radical and Tetrazane[1]

BY FRANCIS OWEN RICE AND FLOYD SCHERBER[2]

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When hydrazine is thermally decomposed at low pressures (~0.5 mm.) and high temperatures (~850°) in a flowing system and the gases leaving the furnace are quickly brought in contact with a liquid nitrogen-cooled finger, a deposit is formed of a bright yellow material, stable indefinitely at −195°; on warming to −178° it decomposes suddenly giving off almost pure nitrogen. Since the material is not paramagnetic, we think it is tetrazane, $H_2NNHNHNH_2$, rather than the hydrazino radical, NH_2NH. The decomposition is probably represented by the equation $H_2NNHNHNH_2 \rightarrow 2NH_3 + N_2$. Preliminary experiments with $H_2N^{15}N^{14}H_2$ indicated that there was at least some randomization of the N_2 formed in the furnace as well as the N_2 formed by decomposition of the yellow substance.

The thermal decomposition of gaseous hydrazine has been studied by several investigators[3] most of whom agree that the thermal decomposition proceeds by a free radical mechanism and is, at least in part, heterogeneous. The homogeneous free radical steps may be represented by the equations

$$N_2H_4 \longrightarrow 2NH_2$$

$$NH_2 + N_2H_4 \longrightarrow NH_3 + NH_2NH$$

We assume that the hydrazino radical decomposes on the wall according to the equation

$$2NH_2NH \longrightarrow 2NH_3 + N_2$$

although collision of NH_2NH either with itself or with NH_2 may be followed by interaction. The intermediate formation of the hydrazino radical in the photochemical decomposition of hydrazine[4] in presence of nitric oxide is strongly suggested by the formation of nitrous oxide as a major product presumably according to the equation

$$NH_2NH + NO \longrightarrow NH_3 + N_2O$$

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(2) Taken from the dissertation presented by Floyd Scherber for the degree of Doctor of Philosophy in The Catholic University of America.

(3) M. Szwarc, *J. Chem. Phys.*, **17**, 505 (1949); P. J. Askey, THIS JOURNAL, **52**, 970 (1930); C. H. Bamford, *Trans. Faraday Soc.*, **35**, 1239 (1939).

(4) C. H. Bamford, *ibid.*, **35**, 568 (1939); see also E. O. Wiig and G. B. Kistiakowsky, THIS JOURNAL, **54**, 1817 (1932).