calorie equal to 4.1840 absolute joules. The ice point is taken to be 273.16°K., and the molecular weight of UO_2Cl_2 as 340.98 g. A 190.623-g. (*in vacuo*) sample of UO_2Cl_2 was used.

The molal heat capacity and thermodynamic functions derived by numerical quadrature from the heat capacity are listed at rounded temperatures in Table II. The heat capacity values were read from a smooth curve through the experimental points, and they are estimated to have a probable error of 0.1% above 25°K., 1% at 10°K. and 8% at 5°K. A Debye T^3 extrapolation was used to obtain values of the thermodynamic functions below 10°K. This formulation yielded heat capacities consistent with the experimental data below 10°K. and assumes the absence of significant thermal anomalies in the extrapolation region below 5.2°K. The effects of nuclear spin and isotope mixing are not included in the entropy and the free energy function. We estimate a probable error in the entropy, heat content and free energy function of 0.1% above 100°K., but in order to make Table II internally consistent, some of the values are given to one more digit than is justified by the estimated probable error.

As a test of the over-all accuracy of the calorimetric process and of the enthalpy increment obtained by integration of the heat capacity, direct determinations of the enthalpy increment were made by measuring the temperature change produced by continuous input of electrical energy. Heating the sample from 47.16 to 79.21°K. required 321.4 cal. deg.$^{-1}$ mole^{-1} and from 78.33 to 249.63°K. required 3492.0 cal. deg.$^{-1}$ mole^{-1}. The values calculated by numerical quadrature of the heat capacity *versus* the temperature yielded 321.2 and 3491.8 cal. deg.$^{-1}$ mole^{-1}, respectively, in excellent agreement with the direct determination.

Discussion

The thermodynamics of the formation of uranyl chloride from the elements at 298.16°K.

$$U(c,\alpha) + O_2(g) + Cl_2(g) \longrightarrow UO_2Cl_2(c)$$

may be evaluated from the standard entropies of uranium,[8] oxygen and chlorine,[9] and the molal free energy of formation of UO_2Cl_2 given by Bozic and Gal.[10] The molal values for $UO_2Cl_2(c)$ at 298.16°K. are

$$\Delta S_f^\circ = -78.34 \pm 0.08 \text{ cal./deg.}$$
$$\Delta F_f^\circ = -277 \text{ kcal.}^{10}$$
$$\Delta H_f^\circ = -300 \text{ kcal.}$$

Acknowledgment.—The support of the U. S. Atomic Energy Commission, the assistance of Mr. George E. Grenier in making the measurements, and of Mrs. Emilia R. Martin with the calculations are gratefully acknowledged.

[8] Reported in: J. J. Katz and E. Rabinowitch, ref. 2, p. 146.

[9] "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Govt. Printing Office, Washington, D. C., 1952.

[10] B. I. Bozic and O. Gal, *Z. anorg. allgem. Chem.*, **273**, 84 (1953). This value is given without any indication of origin or probable error.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE MONSANTO CHEMICAL COMPANY, RESEARCH DEPARTMENT, INORGANIC CHEMICALS DIVISION]

Structure and Properties of the Condensed Phosphates. XI. Hydrolytic Degradation of Graham's Salt

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

RECEIVED APRIL 6, 1956

The initial rate of formation of end groups and of orthophosphate in 1% solutions of Graham's salt, both in the presence and absence of 0.5 *M* NaBr as swamping electrolyte, was measured as a function of *p*H and temperature. Chromatograms run on a series of samples taken during hydrolysis at controlled *p*H values of 4, 7 and 10 were used to help interpret the data. According to the picture developed here, hydrolytic degradation in neutral and alkaline solution consists primarily of scission at the ends of the long chains with concomitant formation of rings (nearly all trimetaphosphate). In acidic solution there is also some random scission along the chain. The presence of rings larger than the tetrametaphosphate and of occasional branching points in Graham's salt is discussed.

A considerable body of evidence[1] has now been built up to show that the vitreous sodium phosphates for which the Na_2O/P_2O_5 mole ratio $\geqslant 1.00$ consist of a distribution[2] of various sized phosphate molecule-ions—for the most part straight chains—with the average chain length increasing as Na_2O/P_2O_5 approaches unity. The term "Graham's Salt" is applied to those glasses (containing large-sized straight-chain phosphates) for which Na_2O/P_2O_5 is exactly one. The exact chain length (number of phosphorus atoms per chain = $\bar{n}$) of a given sample of Graham's salt depends on the residual water left in the $Na_2O \cdot P_2O_5$ glass, since $(\bar{n} + 2)/\bar{n} = (Na_2O + H_2O_{\text{compn.}})/P_2O_5$. Hence, the term Graham's salt refers to a series of glasses exhibiting average chain lengths ranging from a lower value of 30–40 to several hundreds.

This study of the hydrolytic degradation of Graham's salt is a continuation of our more detailed work[3] on the degradation of the pyro- and tripolyphosphates; and, for the most part, identical experimental techniques were used in both investigations. However, this study is not as detailed as

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[1] C. F. Callis, J. R. Van Wazer and P. G. Arvan, *Chem. Revs.*, **54**, 785 (1954).

[2] A quantitative distribution theory and some supporting evidence are given by J. R. Van Wazer, THIS JOURNAL, **72**, 644, 647 (1950), to show that a random reorganization distribution of straight-chain phosphates with an additional small amount of rings gives a first approximation fit to the size distribution of phosphate glasses for which Na_2O/P_2O_5 is approximately unity. Also see paper XII in this series.

[3] J. R. Van Wazer, E. J. Griffith and J. F. McCullough, *ibid.*, **77**, 287 (1955).

the previous one, and it should be considered as a guide to future investigations, rather than as a definitive study of long-chain degradation.

Experimental

The thermostats, *p*H measuring techniques and the analytical procedure[4] for orthophosphate, end groups and middle groups were the same ones used in the previous study.[3] However, this investigation was confined to the sodium system, because with tetramethylammonium ions there was interference with the silver titration for othophosphate in the presence of the Graham's salt. Sodium bromide was used at 0.5 *M* instead of the 0.65 *M* previously[3] employed, because the higher concentration salted out the Graham's salt.

In addition to the analysis[4] based on *p*H titration, paper chromatography was employed to carry out a more complete differential assay on several representative samples. Semi-quantitative two-dimensional chromatography[5] as developed by Ebel and modified by Karl-Kroupa showed how the middle groups were distributed between rings and chains and also gave an independent check on the orthophosphate assay.

In the analytical studies of the rates of hydrolysis, three different preparations of Graham's salt were used. These exhibited average chain lengths, corrected for 10% of the total P_2O_5 as rings, of 110, 125, and (in two runs) 145. These chain lengths were chosen so that there would still be a sufficient number of end groups to be properly analyzed and yet the chains would be representative of very long ones. In repeat analyses where the 125 and 145 chain lengths were employed, there seemed to be no consistent relationship of observed hydrolysis rate with chain length, so no corrections were made for variations in chain length. The samples of Graham's salt were prepared by heating C.P. monosodium orthophosphate in platinum for 1.5 days at 700° and chilling the resulting melt between large plates made from thick (2.5 cm.) copper. According to results obtained by paper chromatography,[5] these glasses contained no detectable orthophosphate (less than 1% of the total P_2O_5) and about 8–11% of the total P_2O_5 in the form of ring phosphates.

In the viscometric studies, a series of glasses having average chain lengths of 59, 78, 95 and 145 were used. They were prepared by the usual technique described above.

Hydrolysis.—In a typical experiment 42.0 g. of Graham's salt was added to 460 ml. of water in a Waring Blendor. After stirring for *ca.* 2 min., all except *ca.* 2 g. of the Graham's salt was dissolved. The resulting solution was then added to 3500 ml. of water heated so that the temperature of the final mixture was very close to that of the hydrolysis experiment. This final mixture had a concentration of 1.00 ± 0.05% $NaPO_3$ by weight. The heated water to which the concentrated phosphate solution was added contained NaOH or HBr to control the *p*H and sometimes contained NaBr, when a swamping electrolyte was needed. Continuous control of the *p*H during the hydrolysis was effected by addition of small portions of concentrated NaOH as the need for such addition was shown by a glass-electrode *p*H meter.

The *p*H titrations[3,4] for weak acid function before and after complete hydrolysis by boiling in strong acid, as well as after addition of silver nitrate, were interpreted as

$$M = 100(s - w)/s \qquad (1)$$

$$O = 100o/s \qquad (2)$$

$$E = 100 - M - O \qquad (3)$$

where M, E and O are the percentages of the total P_2O_5 present as middle groups, end groups, and orthophosphate, respectively; and s, w and o represent the number of equivalents of strong acid function, weak acid function, and orthophosphate, respectively, as measured on a given aliquot. This analysis assumes that the amount of branching-point PO_4-groups[6] in the solution is inappreciably small. The value of M was determined to an absolute accuracy of *ca.* ±0.4%. However, the precision to which this quantity could be measured in a given experiment was usually about ±0.05% of its value, since s was customarily greater than $10w$. The orthophosphate analyses were not nearly as accurate, with irreproducibility between individual measurements of o by the *p*H titration in the presence of silver being 5–10% (and sometimes more) of the value. Furthermore, paper chromatography gave values of o which were about 15–20% higher than those obtained by the *p*H titration in the presence of silver. This means that, although the sum of $O + E$ is correct, O is probably too small and E too large. The rate constants of Table I are presented to the number of significant figures which are believed to represent their reproducibility. The limiting factor in the 90° experiments, especially those at *p*H 4, was the determination of the time, which involved the heating and cooling as well as the handling of the samples.

The rapid initial decrease in reduced viscosity with time which has been found by Strauss,[7] *et al.*, has been reinvestigated under different conditions. In this work a Fisher–Irany viscometer having an efflux time of 484.3 sec. for a 10% solution of tetramethylammonium bromide was employed. The viscosity measurements were made in a small glass thermostat controlled to 30 ± 0.01°, and the initial measurement of viscosity on a freshly prepared sample usually could be completed about 20 min. after the phosphate was first added to the water. When a zero-time intrinsic viscosity was needed, the viscosity data were extrapolated to zero-time. The same zero-time viscosities were obtained whether the extrapolations were carried out on linear (zero-order) or semi-logarithmic (first-order) plots.

Analytical Results.—An example of data obtained by the *p*H titration technique[4] when Graham's salt is hydrolyzed over a long period of time is shown in Fig. 1. In this graph and in Fig. 2, the lines serve to divide the area of the graph into regions reresenting middle groups, end groups and orthophosphate, with each of these three regions being measured in percentage of the total P_2O_5 present in the 1% $NaPO_3$ solution. The middle-group area corresponds to PO_4-groups not at the ends of chains plus those in rings. The net result of the hydrolysis process is to convert middle groups into end groups plus orthophosphate (isolated PO_4-groups). Although the orthophosphate builds up continuously, the increase of end groups is greatest at first and then diminishes until the increase and the concomitant decrease of end groups by hydrolysis into orthophosphate balance each other (at *ca.* 100 hr. in Fig. 1). Thereafter, the total amount of end groups slowly diminishes.

Obviously, the degradation of long-chain phosphates represents an extremely complicated state of affairs when followed to completion. However, the initial hydrolysis ought to be a much simpler process, since, at the beginning of the hydrolysis, the only end groups are those terminating long chains and the preponderant proportion of middle groups are to be found in the long chains. Therefore, this study has been focused on the initial part of the hydrolysis where less than 10% of the middle groups originally present are converted into end groups plus orthophosphate. A typical plot is shown in Fig. 2, where two replicate determinations are represented by the sets of A and B curves, respectively. It should be noted that, in Fig. 2 as well as in 14 similar graphs representing other hydrolysis conditions, the hydrolysis plots were always found to be straight lines for the small amounts of hydrolysis involved. Therefore, the data have been represented as zero-order rate constants in Table I, with the constants being given as the fraction of the total P_2O_5 gained or lost per hour. Such zero-order constants are numerically identical to first-order rate constants fitted to the same data. The rate constant for the build-up of end groups (k_e) is calculated by subtracting the rate constant for the build-up of orthophosphate (k_0) from the constant for the degradation of middle groups (k_M). Naturally, $k_M = k_0 + k_e$, when expressed as zero-order constants. The dashed line labeled Y in Figs. 1 and 2 separates the area of end groups formed by hydrolysis (and hence corresponding to k_e) from the end groups originally present.

Results and Discussion

The kinetic data are presented in Table I, from

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[4] J. R. Van Wazer, E. J. Griffith and J. F. McCullough, *Anal. Chem.*, **26**, 1755 (1954).

[5] E. Karl-Kroupa, *Anal. Chem.*, **28**, 1091 (1956); also see J. P. Ebel, *Bull. soc. chim. France*, **20**, 991, 998 (1953); A. E. R. Westman, A. E. Scott and J. Pedley, *Chem. in Canada*, **4**, 189 (1952).

[6] J. R. Van Wazer and K. A. Holst, THIS JOURNAL, **72**, 639 (1950).

[7] U. P. Strauss, E. H. Smith and P. L. Wineman, *ibid.*, **75**, 3935 (1953); U. P. Strauss and T. L. Treitler, *ibid.*, **77**, 1473 (1955).

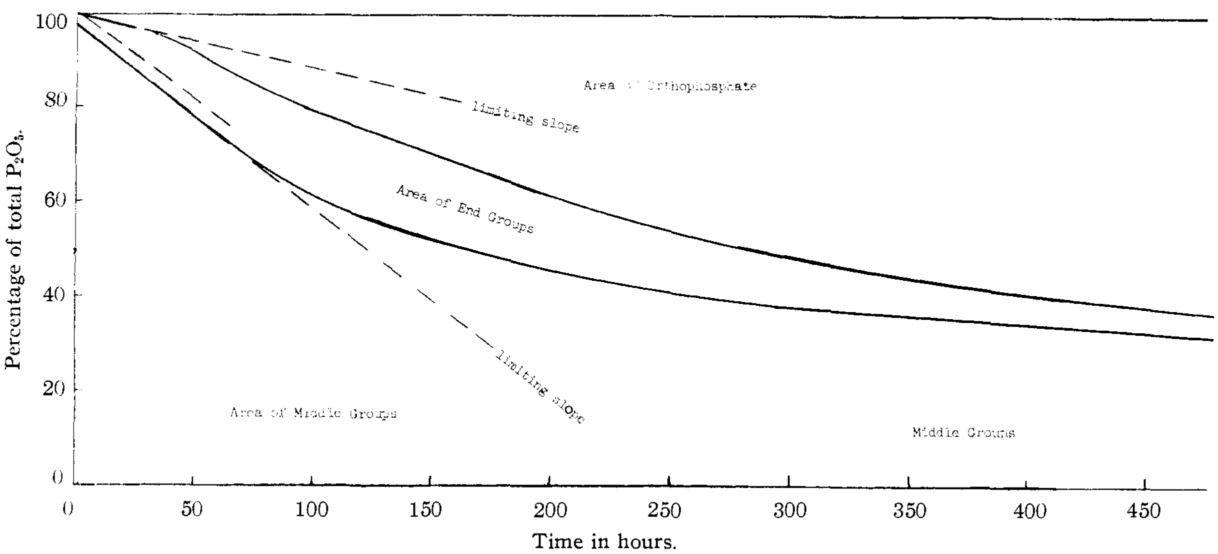

Fig. 1.—Hydrolysis of a 1% solution of Graham's salt ($\bar{n}$ = 125) at *p*H 4 and 60°, with no additional electrolyte. The solid lines in this graph are divisions between middle-group, end-group and orthophosphate areas.

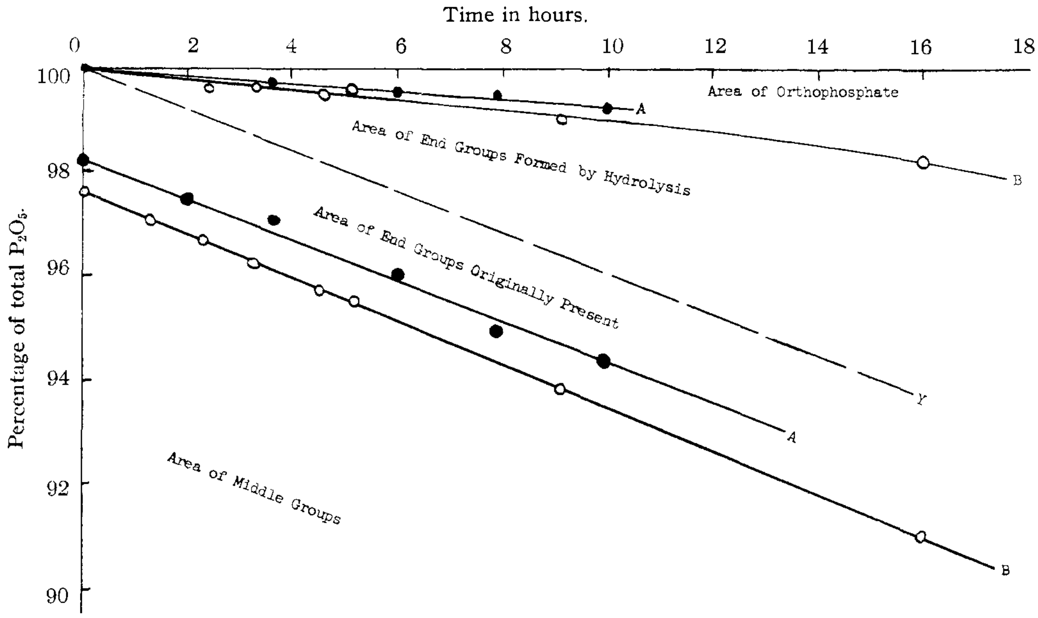

Fig. 2.—Initial hydrolysis of a 1% solution of Graham's salt ($\bar{n}$ = 125 for the A curves and $\bar{n}$ = 110 for the B curves) a *p*H 4 and 60°, with no additional electrolyte.

which it can be seen that the over-all initial rate of hydrolysis, k_M, increases considerably from *p*H 7 to *p*H 4 and does not change much from *p*H 7 to *p*H 10. The rate constants indicate that the stability of the long chains with respect to orthophosphate and end-group formation is the same order of magnitude as that of the pyro- and tripolyphosphates under equivalent experimental conditions. Indeed, for the sodium salts in pure water,[8] the initial degradation of these long chains is slower at each *p*H value than the initial degradation of the pyro- and tripolyphosphates, except for pyro at *p*H 10, when the long-chain degradation is measured by k_M.

The activation energies[9] computed from the rate constants of Table I range from 23 to 30 kcal./mole of P–O–P linkages, with the activation energy for the over-all process usually near 26 kcal./mole of P–O–P linkages. These values differ by *ca.* 4 kcal. or less from those corresponding to similar conditions for pyro- and tripolyphosphate.[3]

The values of k_0 (corresponding to scission at chain ends) regularly decrease with *p*H, either with or without added swamping electrolyte (NaBr). This behavior may be attributed to hydrogen ion catalysis, such as is found for hydrolysis of the pyro-

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(8) Data on the pyro and tripoly from ref. 3 and the following: J. P. Crowther and A. E. R. Westman, *Can. J. Chem.*, **32**, 42 (1954); J. Green, *Ind. Eng. Chem.*, **42**, 1542 (1950); D. O. Campbell and M. L. Kilpatrick, This Journal, **76**, 893 (1954).

(9) Activation energies for hydrolysis of long-chain phosphates from Kurrol's salt were found to lie in the range of 24–26 kcal. by R. Pfanstiel and R. K. Iler, This Journal, **74**, 6059 (1952). For trimetaphosphate rings in alkaline solution (*p*H *ca.* 13), the activation energy is 20 kcal. according to I. A. Brovkina, ref. 15.

TABLE I

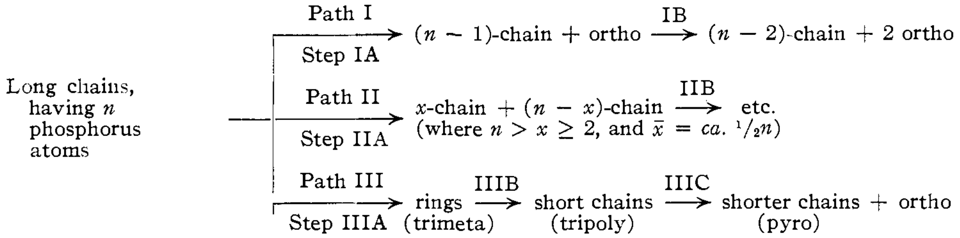
ZERO-ORDER RATE CONSTANTS (IN FRACTION OF TOTAL P_2O_5/HR.) FOR INITIAL HYDROLYSIS OF 1% SOLUTIONS OF GRAHAM'S SALT

Location of scission	Rate constant	pH	30° Pure soln.	30° 0.5M NaBr	60° Pure soln.	60° 0.5 M NaBr	90° Pure soln.	90° 0.5 M NaBr
Over all	k_M	4.0	6.92×10^{-5}	1.90×10^{-5}	3.94×10^{-3}	9.25×10^{-4}	9.0×10^{-2}	2.1×10^{-2}
Chain ends	k_0		1.3×10^{-5}	1.1×10^{-5}	0.9×10^{-3}	6.4×10^{-4}	4.6×10^{-2}	1.3×10^{-2}
Not at ends	k_e		5.6×10^{-5}	0.8×10^{-5}	3.0×10^{-3}	2.9×10^{-4}	4.4×10^{-2}	0.8×10^{-2}
	k_0/k_e		0.2	1.4	0.3	2.2	1.0	1.7
Over all	k_M	7.0	5.50×10^{-6}		2.35×10^{-4}	2.91×10^{-4}	8.1×10^{-3}	9.2×10^{-3}
Chain ends	k_0		4.9×10^{-6}		1.7×10^{-4}	2.2×10^{-4}	6.2×10^{-3}	8.2×10^{-3}
Not at ends	k_e		0.6×10^{-6}		0.7×10^{-4}	ca. 7×10^{-4}	1.9×10^{-3}	1.0×10^{-3}
	k_0/k_e		8.1		2.4	0.3 (?)	3.3	8.2 (?)
Over all	k_M	10.0			3.35×10^{-4}	7.92×10^{-4}	8.8×10^{-3}	3.0×10^{-2}
Chain ends	k_0				1.1×10^{-4}	1.6×10^{-4}	4.9×10^{-3}	0.9×10^{-2}
Not at ends	k_e				2.3×10^{-4}	6.3×10^{-4}	3.9×10^{-3}	2.2×10^{-2}
	k_0/k_e				0.5	0.3	1.2	0.4

and tripolyphosphates.[3] In acid solution, the addition of swamping electrolyte causes a decrease in k_0 as predicted by the Brönsted-Bjerrum rule[10] for acid catalysis of an anion. Reversal of this effect at pH values greater than *ca.* 5 does not indicate base catalysis but is quite probably due to sodium catalysis, as previously described.[3] The reversal occurs at a lower pH of *ca.* 2–3 in the case of pyro- and tripolyphosphates, so that it appears that the binding of hydrogen as compared to that of sodium is greater for the longer chains. In addition, the change in rate constants upon adding the swamping electrolyte is more pronounced in the case of the long chains. This result is in accord with studies[11] of complexing in which the long chains are shown to exhibit better sodium- and hydrogen-binding capacity than the short-chain phosphates.

The values of k_e (corresponding to scission of P–O–P linkages in rings or at positions in chains other than at the ends) go through a pronounced minimum (down 10- to 100-fold) at pH 7—a behavior which is probably due to the presence of both acid and base catalysis. The effect of swamping electrolyte supports this conclusion, since adding the electrolyte causes a pronounced decrease in hydrolysis rate at pH 4 and a significant increase at pH 10. At pH 7, the effect of added electrolyte is relatively small.

Due primarily to the work of Thilo,[12,13] it is now well recognized that, during the hydrolytic degradation of long-chain phosphates, there is an appreciable build-up of rings (mostly trimetaphosphate but also some tetrametaphosphate). This means that there are three alternative degradation paths, which may be interrelated or may occur simultaneously. These paths, shown below, are I, splitting off of end groups; II, random scission along the chain; and III, ring formation.



Chromatographic studies demonstrate that, at pH 7, approximately equal quantities of phosphorus are converted to trimetaphosphate and to orthophosphate during the initial period on which *ca.* 15% of the total P_2O_5 appears as orthophosphate. During the same period, there is no increase in the amount of larger rings and no detectable formation of the shorter chains containing from 2 to 10 phosphorus atoms. This means that equal numbers of phosphorus atoms degrade by paths I and III given above, with no degradation occurring by path II in the neutral pH region. At very alkaline pH values, the trimetaphosphate does not build up because it is unstable and rapidly degrades to tripolyphosphate as quickly as it is formed. These findings are in accord with data[14,15] on the rapid alkaline cleavage of ring phosphates, the hydrolytic degradation of which appears to be base catalyzed.

At pH 10, about 3 moles of phosphorus is converted into trimetaphosphate per mole of orthophosphate formed, during the period in which *ca.* 10% of the total phosphorus is converted into orthophosphate. The number of moles of phosphorus going into tetrametaphosphate nearly equals the number of moles of orthophosphate. There is some tripolyphosphate formed along with lesser amounts of pyro- and even smaller quantities of tetrapoly-

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

[11] F. T. Wall and R. H. Doremus, THIS JOURNAL, **76**, 868 (1954) V. Schindewolf, *Z. physik. Chem.*, **1**, 134 (1953); J. R. Van Wazer and K. A. Holst, THIS JOURNAL, **72**, 639 (1950).

[12] Original experimental data from R. N. Bell, *Ind. Eng. Chem.*, **39**, 136 (1947).

[13] Recognized and reconfirmed by E. Thilo, *Chem. Technik*, **4**, 345 (1952); and E. Thilo, G. Schulz and E. Wichmann, *Z. anorg. allgem. Chem.*, **272**, 182 (1953). Information about tetrametaphosphate build-up comes from a private communication with E. Thilo.

[14] I. A. Brovkina, *J. Gen. Chem.* (*U.S.S.R.*), **22**, 1917 (1953).

[15] J. Crowther and A. E. R. Westman, *Can. J. Chem.* (in press).

and pentapolyphosphates. The number of moles of phosphorus converted into the sum of these chain phosphates is slightly less than the number of moles of orthophosphate produced during the same period. These results we tentatively attribute to base catalysis of step IIIA. This assumes that sodium-ion catalysis is not important, and that the chain phosphates come from ring scission, *via* step IIIB. More study is needed here.

In acid solution, the picture is changed considerably, as shown by the chromatographic data presented in Fig. 3. As in neutral solution, approximately equal quantities of phosphorus originally present in the long chains are changed into trimetaphosphate and into orthophosphate, during the period in which *ca.* 15% of the total phosphorus is converted into orthophosphate. There is also considerable build-up of chains (and/or large rings) containing from 6 to *ca.* 15 phosphorus atoms apiece. This is accompanied by a noticeable increase in the individually measured chains containing from two to five phosphorus atoms. There is a slight increase in the amount of intermediate sized rings containing four and five phosphorus atoms apiece. These data indicate that paths I, II and III are all employed in acid degradation—with roughly the same number of phosphorus atoms following each path.

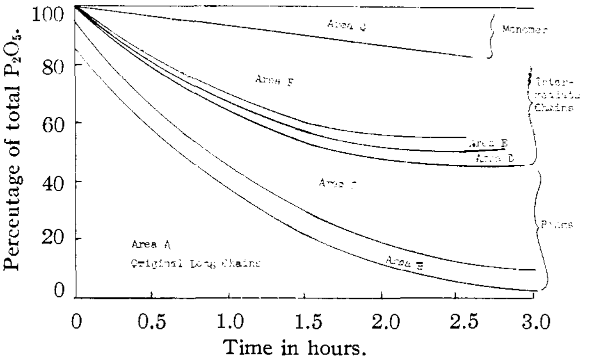

Fig. 3.—Chromatographic results obtained by hydrolyzing Graham's salt at *p*H 4 and 90°: Area A = long-chain phosphates (non-moving in the chromatogram); B = ring metaphosphates containing 4 to 6 phosphorus atoms; C = trimetaphosphate; D = pyrophosphate; E = tripolyphosphate; F = chain phosphates (polyphosphates) containing 4 to 15 phosphorus atoms plus any rings made up of more than 6 phosphorus atoms; and G = orthophosphate.

Steps IA, IB, IC, etc., in the degradation of long-chain phosphates, are acid catalyzed and play an important role in the hydrolysis process at all values of the *p*H. These steps contribute nearly all of the observed build-up of orthophosphate in neutral and basic media and play an important role in acid media. The rate constant k_0 is thus primarily dependent on these terminal scission steps. Step IIIA is also fast at all values of the *p*H and is thought to be both acid and base catalyzed; whereas, step IIIB is extremely slow[15] in the *p*H range from 5 to 9 but increases rapidly in more acidic or basic media because of the very pronounced acid and base[16] catalysis. Step IIIC is acid and sodium-ion catalyzed, as previously discussed.[3] It is slow, except at low values of the *p*H. Steps IIA, IIB, etc.—corresponding to random scission in the long chains—are very slow, except in acid media, where they do not dominate the overall reaction. Presumably, the acid catalysis of the rate constant, k_e, for the build-up of ends receives its greatest contribution from path II in the acidic range and from path III, steps IIIA and especially IIIB, in the basic range.

As shown by Table I, our measured values of k_0/k_e lie in the range[15] of 0.1 to 10. Since the ratio of end groups to middle groups in the chain phosphates studied varied from 14/1000 to 19/1000, we must conclude that scission at the ends of the chains proceeds from ten- to a thousandfold faster than elsewhere in the chains, with the smaller number corresponding to acidic conditions. This conclusion is in accord with the findings of Crowther and Westman,[15] who have recently shown that degradation of the tetrapolyphosphate ion is nearly all attributable to end-group scission, and that this scission is severalfold more rapid than scission of either of the P–O–P linkages in the tripolyphosphate anion. Tripolyphosphate is also known[3] to degrade faster than the pyrophosphate. By generalizing on the small amount of available data, one can conclude that the longer the chain, the faster the scission of terminal groups. In spite of this, long-chain phosphates are reasonably stable as compared to short chains in the region of neutral *p*H, because there are very few end groups as compared to middle groups in solutions of long-chain phosphates.

Related Data

As has been recently noted,[17] ring phosphates larger than the tetrametaphosphates can be found in solutions of Graham's salt. Although we have not yet been able to produce isolated spots for heptametaphosphates and larger rings on a chromatogram, there is a streak leading from the origin to the series of spots corresponding to hexameta-, pentameta-, tetrameta- and trimetaphosphates, so that one would guess that a complete homologous series of ring phosphates ranging from the trimeta to very large rings exists in Graham's salt. In a freshly dissolved sample of Graham's salt for which $\bar{n}_{cor}$ = 100–125, there is about 3.9% trimeta, 2.5% tetrameta, 0.75% pentameta, 0.5% hexameta, and apparently lesser amounts of each of the larger rings. The barium precipitation procedure (Jones method[18] as applied by Dewald[19]), and solubility fractionation[20] show 7.7 ± 0.2% and 6.5 ± 0.5% ring phosphate (called trimetaphosphate), respectively, in fresh solutions of Graham's salt. Apparently, rings containing more than four or five phosphorus atoms cannot be distinguished from chains by these two procedures.

The initial rapid drop in dilute solution viscosity of Graham's salt, which were discovered by Strauss[7] and attributed by him to occasional

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(16) There is a very remote possibility that this might be sodium-ion catalysis.

(17) J. R. Van Wazer and E. Karl-Kroupa, This Journal, **78**, 1772 (1956).

(18) L. T. Jones, *Ind. Eng. Chem., Anal. Ed.*, **14**, 536 (1942).

(19) W. Dewald and H. Schmidt, *Z. anorg. allgem. Chem.*, **272**, 253 (1953). Also private communications from Dewald.

(20) J. R. Van Wazer, This Journal, **72**, 647 (1950).

branching (about 1 PO_4-group/1000 is a branching point), was investigated as a function of chain length. In this work, the conditions which one of us employed in the first viscometric study[21] (Paper V of this series) of a series of chain phosphates of varying length were repeated. The results are shown in Fig. 4. According to the new data, the branching becomes undetectably small when the number average chain length is reduced below *ca.* 50. Apparently, the formation of branches represents a gradual approach to the ultraphosphate region[22] as Na_2O/P_2O_5 is reduced from values greater than one. The data of Fig. 4 give added support to Strauss' contention that the initially high viscosity is not due to the effect of impurities.

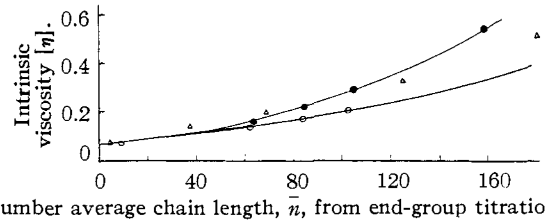

Fig. 4.—Variation of intrinsic viscosity of slightly branched and straight-chain phosphates from Na_2O/P_2O_5 glasses as a function of chain length. Zero-time extrapolated values for chains with some branching denoted by black circles; values after 12 hr. standing (with chain lengths corrected for ortho) by open circles; and the now obsolete data from Paper V[17] by triangles.

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[21] J. R. Van Wazer, THIS JOURNAL, **72**, 906 (1950). The results of Fig. 4 should be substituted for those in Paper V.

[22] J. R. Van Wazer and E. J. Griffith, *ibid.*, **77**, 6140 (1955).

[CONTRIBUTION FROM THE FRANKLIN INSTITUTE LABORATORIES FOR RESEARCH AND DEVELOPMENT]

Heats of Adsorption of Oxygen on Nickel, Platinum and Silver[1]

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The adsorption thermodynamics of oxygen was studied on powdered nickel, platinum and silver samples in the temperature range 150–300°. and surface coverages in the range 10^{-4} to 10^{-3}. Data were obtained by means of decomposition equilibria of water vapor on the surfaces concerned. Values for the heat of oxygen adsorption on nickel were found to be similar to those related to the formation of bulk nickel oxide. On the other hand, large differences between surface and bulk heat values were found for platinum and silver. Similarly, the value of the adsorption equilibrium constant for oxygen was found to increase with increasing surface coverage on nickel, while the same quantity was found to decrease with increasing surface coverage on platinum and silver. These effects are interpreted in terms of current models of the adsorption process. For the same temperature range, no oxygen chemisorption could be detected on powdered gold.

A knowledge of the thermodynamic affinity of solid surfaces is important not only in respect to the formulation of a theory of catalytic action, but also in regard to the more fundamental problem of the physico-chemical properties of solid surfaces. Oxygen is known to combine by forming a bond, with practically all metal surfaces. Consequently, this bond should not be too dependent upon the detailed electronic structure of the metal, as is the case for hydrogen. Oxygen affinities, however, show considerable variations among metallic surfaces. In order to have more information on the important factors which control the interaction of a metal surface with oxygen, we have investigated the thermodynamics of oxygen chemisorption on three different metal surfaces. Furthermore, it is of interest to examine surface affinities in the light of the well known bulk affinities for oxygen. From such a comparison, a contribution can be made toward the goal of understanding surface behavior in terms of bulk properties. Finally, the catalytic activation of molecular oxygen, through chemisorption, is a necessary prerequisite to a large number of oxidation reactions, and the steady-state configuration of the catalytic surface is, under these conditions, largely determined by its thermodynamic affinity for oxygen.

In the present work, thermodynamic quantities for chemisorption have been derived by means of the adsorption equilibrium function. This is given by

$$K = \frac{\text{Activity of occupied sites}}{\text{Activity of vacant sites} \times \text{activity of adsorbate mols.}}$$

It has been shown that K varies in a characteristic manner with conditions at the surface during adsorption.[3] If the activity coefficients for vacant and unoccupied sites are assumed equal, the above equation becomes

$$K = \frac{\theta}{(1 - \theta) \times C}$$

where θ is the fraction of surface covered and C is the activity of free molecules. The quantity K is independent of θ only for the case of localized, non-interacting adsorbed molecules. Since $RT \ln K = -\Delta F^{\circ}$, the equilibrium constant can be related to the free energy change, resulting from the transfer of one mole of free adsorbate molecules, at their standard state, to the adsorbed layer at the standard state. K is thus representative of the nature of the adsorption bond. The quantity ΔF°, and consequently K increases with increasing

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[3] D. Graham, *J. Phys. Chem.*, **57**, 665 (1953).