[CONTRIBUTION FROM MONSANTO CHEMICAL COMPANY, RESEARCH DEPARTMENT, INORGANIC CHEMICALS DIVISION, ST. LOUIS, MISSOURI]

Principles of Phosphorus Chemistry. X. Reorganization ot Polyphosphorus Compounds: the Phosphoryldimethylamides[1]

BY EINHARD SCHWARZMANN[2] AND JOHN R. VAN WAZER

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The phosphoryldimethylamide family of un-ionized compounds has been prepared by reorganizing various proportions of hexamethylphosphorylamide with phosphorus pentoxide at 160°. The compounds in this family exhibit one nonbridging oxygen atom for each phosphorus atom, with phosphorus atoms being connected to each other through oxygen bridges. The remainder of the four coördination sites per phosphorus are filled by dimethylamido groups. In accord with previous publications in this series, structural reorganization between the various phosphoryldimethylamides can be partially described in terms of equilibria between the monophosphorus compound and the end-group, middle-group and branching structural units. The constant describing the equilibrium in which two middle groups react to form an end and a branching group was found to be equal to 6×10^{-4} at 158°. At the same temperature the equilibrium constant for the reaction whereby two end groups form the monophosphorus compound and a middle group was equal to 0.026. In addition to isolation of the ortho, pyro, tripoly and trimeta molecules, rapid solubility fractionation by adding acetone to an aqueous solution of the unhydrolyzed composition showed, *via* light scattering, that there is a distribution of high-molecular-weight species at the metaphosphoryl composition. As in previous studies from this Laboratory, nuclear magnetic resonance was used to determine the amounts and kinds of structural building units.

Structural reorganization of monophosphorus compounds, such as described in Papers V,[3] VI, VIII and IX[4] of this series, occurs through exchange of monofunctional ligands (say X and Z) between phosphorus atoms so as to form all possible combinations (ΞPX_3, ΞPX_2Z, ΞPXZ_2 and ΞPZ_3, where Ξ is an electron-pair-acceptor atom or group or an unshared pair of electrons). This process can be extended to molecules or molecule-ions based on more than one phosphorus atom by letting X and/or Z be a polyfunctional ligand. In this paper and in a preceding one,[5] cases are discussed in which Z stands for a bridging oxygen atom and X represents the $-N(CH_3)_2$ group or chlorine, $-Cl$, respectively—with Ξ being a nonbridging oxygen atom. The series of compounds corresponding to $X = -N(CH_3)_2$, $Z = -O-$ and $\Xi = -O$ can be called (poly)-phosphoryldimethylamides.

The first member of this series of compounds, hexamethylphosphorylamide, has long been known and the second member, the pyro compound, was first described by Schrader.[6] In addition, the ethyl analog of the six-atom ring compound, hexaethyltrimetaphosphorylamide, had previously been isolated as a crystalline species.[7] The literature also describes preparations of the tripoly-[8,9] and isotetrapolyphosphoryldimethylamide molecules.[8] As will be shown later in this paper, all of these preparations except for the ortho and trimeta compounds correspond to the reorganization-equilibrium mixture exhibiting the same empirical composition as the pure compound alleged to have been obtained.

Experimental Operations

This paper demonstrates the applicability to the family of phosphoryldimethylamides of the method of making intermediate species between the monophosphorus compound and the completely branched structure by combining these end members in various proportions. In doing this, doubly distilled hexamethylphosphorylamide was mixed with C. P. phosphorus pentoxide and heated in rocking, thick-walled Pyrex tubes at 160 or 80° for a week longer than the minimum length of time needed to achieve equilibrium. At the end of this period, the tubes were removed from the oven and allowed to cool in air. Since it took more than a week at 26° and several hours at 100° before a slight change in composition could be detected in nonequilibrium preparations reorganizing to equilibrium, the cooling time of *ca.* 10 min. to go from 160 to 40° was thought to be sufficiently rapid to freeze in the equilibrium at a temperature corresponding to $158 \pm 2°$.

Nuclear magnetic resonance (n.m.r.) data on pilot samples heated at 160° for various lengths of time indicated that for the composition parameter[13] $R = (CH_3)_2N/P$ mole ratios ranging from 2.8 to 1.3, equilibrium is achieved in three to seven days. (Note: R is *not* an alkyl group.) For $0.9 \leq R < 1.3$, several weeks are needed. For values of R less than 0.9, a homogeneous solution of the phosphorus pentoxide in the hexamethylphosphorylamide was never achieved. Apparently the rate of a side-reaction decomposition is faster than the rate of reorganization in this composition range. For example, when a sample for which $R = 0.5$ was heated at 200°, it took about three months to achieve a homogeneous appearance, at which time the resulting material was a dark brown solid and gas pressure was observed upon opening the tube. In the case of the reorganization equilibria at values of $R > 0.9$, no pressure build-up due to gas formation was observed at 160°. As might be expected, considerably higher temperatures (230°) gave much decomposition with gas evolution in relatively short heating periods.

The P^{31} n.m.r. technique was the same as previously described[3] except that linearity corrections were not employed. As a check on the method, the n.m.r. pattern of the various pure species was obtained in carbon tetrachloride and in the pure liquid state. The chemical shifts for the various pure liquids and their solutions were found to agree within 1 p.p.m. of the magnetic field; and the relative peak areas, when there was more than one resonance, agreed within experimental error. This was also found to be true for the

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[2] On leave of absence during 1959 from Göttingen University, Germany.

[3] L. C. D. Groenweghe and J. H. Payne, THIS JOURNAL, **81**, 6357 (1959).

[4] J. R. Van Wazer and E. Fluck, *ibid.*, **81**, 6360 (1959); E. Fluck, J. R. Van Wazer and L. C. D. Groenweghe, *ibid.*, **81**, 6363 (1959); E. Schwarzmann, *ibid.*, **81**, 6366 (1959). For earlier work see G. Calingaert and H. A. Beatty, *ibid.*, **61**, 2749 (1939); G. Calingaert, H. A. Beatty and H. R. Neal, *ibid.*, **61**, 2755 (1939); G. Calingaert and H. Saroos, *ibid.*, **61**, 2759 (1939); and R. N. Fuoss, *ibid.*, **65**, 2506 (1943).

[5] L. C. D. Groenweghe, J. H. Payne and J. R. Van Wazer, *ibid.*, **82**, 5305 (1960).

[6] G. Schrader, *Die Entwicklung neuer Insektizide auf der Grundlage organischer Fluor und Phosphor-Verbindungen*, Verlag Chemie, Weinheim, 1952; also see D. W. Pound and B. C. Saunders, Brit. Pat. 631,-549 (1949); G. S. Hartley, D. F. Heath, J. M. Hulme, D. W. Pound and M. Whittaker, *J. Sci. Food Agr.*, **2**, 303 (1951).

[7] A. Michaelis, *Liebig's Ann.*, **326**, 191 (1903).

[8] H. Tolkmith, THIS JOURNAL, **75**, 5270 (1953); *ibid.*, **75**, 5273 (1953); *ibid.*, **75**, 5276 (1953).

[9] W. T. Dye, U. S. Patent 2,610, 139(1953); M. Pianka, *J. Appl. Chem.*, **5**, 109 (1955).

random-reorganization mixtures for which $R > 1.1$. Fine structure due to indirect spin–spin splitting by neighboring phosphorus atoms was not seen in most measurements. However, extremely high resolution showed a complex fine structure attributable to indirect spin–spin splitting by the hydrogen of the methyl groups as well as spin–spin interaction between phosphorus atoms in structurally different positions.

Solubility-fractionation studies were carried out by preparing a 23% solution in water at 25° of the reorganization mixture for which $R = 1.0$. It was found that 0.9 wt.-% of the sample, consisting of a blackish impurity, did not dissolve. After six passes through a Millipore filter, light-scattering measurements were made at concentrations of 1, 0.5, and 0.25%. Then 30 ml. of acetone was gradually added to 130 g. of the sample in order to obtain sufficient precipitation to give the first fraction, which appeared as a viscid, dark brown oil after removal of water and acetone under vacuum. Addition of 25 more ml. of acetone gave the second fraction, and addition of 5 more ml. gave the third fraction. The residuum, after removal of water and acetone under a vacuum at room temperature, was a light yellow substance considerably less viscous than the first fraction. The light-scattering molecular weights were determined on all fractions and the original sample by using the Brice–Phoenix light-scattering photometer in combination with the differential refractometer manufactured by the same company. The standard Debye equation[10] was employed and asymmetry measurements were not made because of lack of time, since the measurements were carried out rapidly to avoid hydrolysis.

The usual two-dimensional paper chromatography as described by Karl-Kroupa[11] was employed on aqueous solutions. The unhydrolyzed phosphoryldimethylamide compounds were all found to move with the solvent front so that they did not appear on the chromatograms which showed only the products of hydrolysis.

Two stills were used in this study. One was a regular vacuum unit with a short fractionating column, and the other was a pot-type molecular still having a large cold-finger condenser. Evacuation of this latter still was accomplished by a mercury-diffusion pump through a large-diameter glass tube.

Data and Interpretation for Mixtures

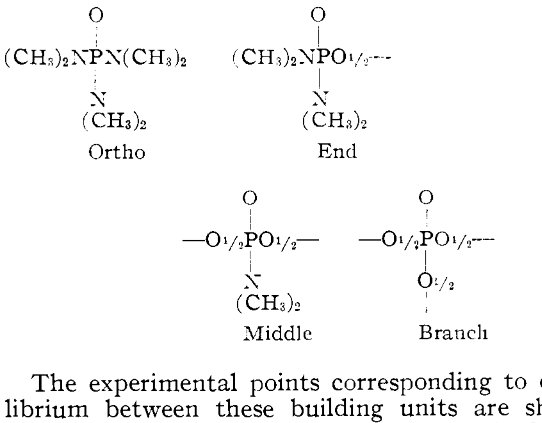
Physical Properties.—The equilibrium mixtures exhibit the variations in physical properties to be expected from the theory[12,13] of structural reorganizations involving interchange of functionality of the structural building units. For values of $R = (CH_3)_2N/P$ lying between 3 and 1.5, the mixtures are all relatively fluid. From $R = 1.5$ to $R = 1.3$, there is a noticeable increase in viscosity, which rises rapidly as R drops from 1.3 to 1.1. At $R = 1.1$, the material exhibits a rubbery appearance and, as R decreases to 0.95, the properties change in the same way as do those of rubber with increased vulcanization. In the range from 0.95 to 0.7 and presumably all the way to $R = 0$, the reorganization mixtures are glassy. The transition between the glassy and rubberlike behavior at room temperature is found, within experimental error, to occur at 97% of the value of R below which infinitely branched structures exist.[14]

In the range of $0.97 \leqslant R \leqslant 3$, all reorganization mixtures could be dissolved in carbon tetrachloride within a few minutes at 100° without appreciable reorganization between structural building units being detected by nuclear magnetic resonance. Again, the critical value of $R = 0.97$ appears to be close to the point below which infinitely branched structures are expected, *i.e.*, the gel point. At room temperature, n.m.r. showed that appreciable reorganization between structural building units of the phosphoryldimethylamide compounds dissolved in carbon tetrachloride does not occur in a period of several weeks, if the heating were not prolonged beyond the short time needed for dissolution.

The reorganization mixtures, either before or after reaching equilibrium, as well as the various pure species prepared were all highly soluble in water. Electrical-conductivity measurements showed that the compositions not containing branching points did not react immediately with water at room temperature or below.

Reorganization of Structural Units.—Only four significant peaks were found in the n.m.r. traces—with the exact resonance position of a given peak varying within a range of 2 p.p.m. or less of the magnetic field, depending on the value of R. Material balances for various values of R unequivocally demonstrated the following assignments: the ortho compound (hexamethylphosphorylamide), −23 p.p.m.; end structural unit, −11.5 p.p.m.; middle structural unit, 12.0 p.p.m.; branch structural unit 40 p.p.m. These chemical shifts are referred to a standard consisting of 85% H_3PO_4, with the positive direction of shifts being upfield. The observed chemical shift for hexamethylphosphorylamide agrees well with the value of −23.4 p.p.m. reported by Muller, Lauterbur and Goldenson,[15] the value of −27 given by Van Wazer, Callis, Shoolery and Jones[16] obviously being only an approximation. The end-group resonance was found to be in agreement with the reported values[16] of −11 and −12 p.p.m.

The various structural building units described above exhibit the following stoichiometry, where $O_{1/2}$ represents an oxygen shared between two neighboring phosphorus atoms.



$$\underset{\text{Ortho}}{(CH_3)_2N\overset{O}{\underset{\underset{(CH_3)_2}{N}}{P}}N(CH_3)_2} \qquad \underset{\text{End}}{(CH_3)_2N\overset{O}{\underset{\underset{(CH_3)_2}{N}}{P}}O_{1/2}—}$$

$$\underset{\text{Middle}}{—O_{1/2}\overset{O}{\underset{\underset{(CH_3)_2}{N}}{P}}O_{1/2}—} \qquad \underset{\text{Branch}}{—O_{1/2}\overset{O}{\underset{O_{1/2}}{P}}O_{1/2}—} \qquad (1)$$

The experimental points corresponding to equilibrium between these building units are shown in Fig. 1. From the values given in this figure, the equilibrium constants have been computed:

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[10] P. Debye, *J. Appl. Phys.*, **15**, 338 (1944).

[11] E. Karl-Kroupa, *Anal. Chem.*, **28**, 1091 (1956).

[12] J. R. Parks and J. R. Van Wazer, THIS JOURNAL, **79**, 4890 (1957); J. R. Van Wazer, *ibid.*, **72**, 644 (1950).

[13] J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. I, Interscience Publishing Co., New York, N. Y., 1958, Chapter 12.

[14] Calculation of the value of R below which infinitely branched structures should appear was done on an IBM 704 computer set up to carry out calculations equivalent to sorting structural building blocks into molecules. In this sorting process no provision was made to include either simple or fused rings in the infinite structures, *i.e.*, there is only one path in a molecule from one branch to another.

[15] N. Muller, P. C. Lauterbur and J. Goldenson, THIS JOURNAL, **78**, 3557 (1956).

[16] J. R. Van Wazer, C. F. Callis, J. N. Shoolery and R. C. Jones, *ibid.*, **78**, 5715 (1956).

$$K_1 = \text{[end groups][branching groups]/[middle groups]}^2 = \frac{e \cdot b}{m^2} = (6 \pm 2) \times 10^{-4} \quad (2)$$

$$K_2 = \text{[ortho structure][middle groups]/[end groups]}^2 = \frac{o \cdot m}{e^2} = (2.6 \pm 0.3) \times 10^{-2} \quad (3)$$

Since the same results were obtained for equilibration temperatures of 158 and 80°, it appears that the enthalpy of reorganization is small (<*ca.* 1 kcal.).

Solubility Fractionation.—By using acetone as the precipitant, a freshly prepared aqueous solution of a reorganized mixture for which $R = 0.98$ was fractionated. The average molecular weight obtained by light scattering immediately after dissolution corresponded to 510 phosphorus atoms per molecule. After rapid fractionation, the molecular species were distributed so that the first fraction, which consisted of 22% of the total phosphorus, corresponded to an average molecule containing 800 phosphorus atoms. The second fraction (36% of the total P) corresponded to 610 phosphorus atoms per molecule, the third fraction (16%) to a 390 P/molecule and the residuum (26%) to a 134 P/molecule. The least accurate of these molecular-size values is, of course, the one corresponding to the low-molecular-weight residuum.

The n.m.r. data show that 96.3% of the total phosphorus was present as middle groups, 3.3% as branches and *ca.* 0.4% as end groups in the unfractionated mixture before dissolution. This corresponds to an infinite number-average number, $\bar{n}_\Sigma$, of phosphorus atoms per molecule, according to the equation

$$\bar{n}_\Sigma = (o + e + m + b)/(o + e/2 - b/2) \quad (4)$$

where e, m and b are percentages of the total phosphorus as ends, middles and branches respectively, and minus values of $\bar{n}_\Sigma$ correspond to infinite structures.

Upon complete hydrolytic degradation of only the branches, each b becomes an m and the b, m or e forming the other end of the ruptured P–O–P linkage becomes an m, e or o respectively. In the case where there is a preponderance of middles, the ruptured P–O–P linkages will be predominantly between branches and middles and equation 4 becomes

$$\bar{n}_\Sigma' = (o + e + m + b)/(o + e/2 + b/2) \quad (5)$$

where $\bar{n}_\Sigma'$ is the number-average number of phosphorus atoms per molecule *after* hydrolysis of all branches, b, originally present.

Since the value of $\bar{n}_\Sigma'$ for the composition under study is calculated to be 54 from equation 5, it is apparent that only about half of the branch points hydrolyzed upon dissolution. Presumably the other half were protected by stearic hindrance.

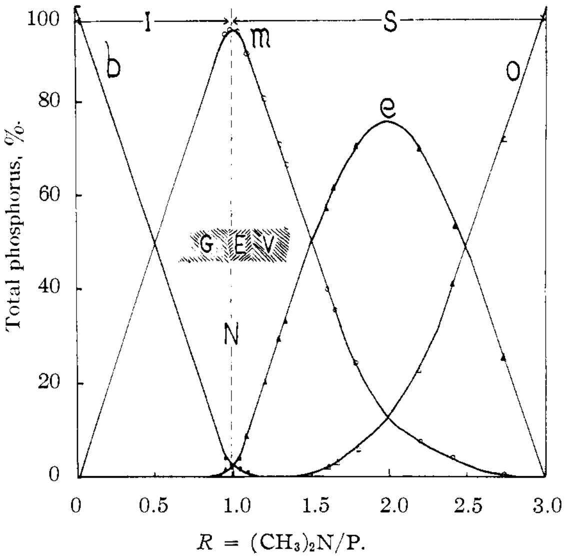

Fig. 1.—Equilibrium between structural building units in the system $[(CH_3)_2N]_3PO—P_2O_5$ at 158°. The symbol o stands for the ortho compound (hexamethylphosphorylamide); e for end groups; m for middle groups; and b for branching groups. For values of R less than N, infinite-network polymers should exist. V stands for the range of R-values in which the system exhibits high viscosities at room temperature, E for the region of rubber-like elasticities; and G for the glassy region (down to $R = 0$). The composition range denoted by S corresponds to solubility in hot carbon tetrachloride; I stands for insolubility in this solvent.

Hydrolysis.—Reorganization-equilibrium mixtures were hydrolyzed for various lengths of time at 60° and *p*H 1, with the resulting hydrolysates being investigated by Ebel's two-dimensional paper-chromatographic procedure[11] for phosphates. It was found that the unhydrolyzed phosphoryldimethylamides gave no chromatographic spots since they appeared to move with the solvent front. Upon continuing hydrolysis of mixtures exhibiting R values near unity, non-moving phosphate first appears on the chromatograms and is gradually displaced by lower-molecular-weight species in which the trimetaphosphate predominates. About a quarter of the total phosphorus appears in the form of trimetaphosphate at the time when this species maximizes in the course of hydrolysis of the only slightly branched high-molecular-weight polyphosphoryldimethylamides.

These chromatographic measurements indicate that P–N bonds hydrolyze faster than do the P–O–P linkages. Furthermore the build-up of trimetaphosphate shows that rings form concomitantly with P–O–P scission in the hydrolysis of the long-chain polyphosphoryldimethylamides just as they do in the hydrolysis of long-chain polyphosphates.[17] The chromatographic work reported here was not sufficiently precise to determine whether or not there is formation of considerably lesser amounts of rings larger than the trimetaphosphate, as is observed in the hydrolysis of the long-chain phosphates.[17]

Exploratory hydrolysis studies of reorganization-equilibrium mixtures having R values between 1.25 and 2.2 showed that short-chain phosphate ions could be picked up on the chromatograms. When interpreted in light of the available data on phosphate hydrolyses,[17,18] the results were found to be in qualitative agreement with the concept of the average chain length increasing as the ratio of middle to end structural units becomes larger.

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[17] J. F. McCullough, J. R. Van Wazer and E. J. Griffith, THIS JOURNAL, **78**, 4528 (1956).

[18] See pp. 452–459 of ref. 13.

Both electrical conductivity and paper chromatography were used in preliminary investigations of hydrolysis rate. The ring compound exhibited the fastest hydrolysis of all the unbranched species. At 25° and *p*H 7, the approximate half life of the pure trimeta compound is 0.5 hr. Under the same conditions, the half lives of the unbranched mixtures ($1.1 \leqslant R \leqslant 3$) were large—at least several weeks. At 60° and *p*H 1, the approximate half lives for hydrolysis of the reorganization mixtures for which $1.1 \leqslant R \leqslant 3$ ranged from about several weeks for $R = 3$ to about three days for $R = 2$ and to only a few minutes for $R = 1.1$. Branching points were found to be sites of especially rapid hydrolysis, as in the phosphate salts.[18]

Data and Interpretation for Pure Compounds

Distillation.—The ortho and pyro species (hexamethylphosphorylamide and octamethylpyrophosphorylamide) can be cleanly separated from each other and from the various reorganization-equilibrium mixtures by low-temperature distillation under increasing vacuum. Under our conditions the ortho compound distilled at 26–27° and the pyro at 29–30°. Between 30 and 80° with a good vacuum, nothing was found to come over; and, in the range of 80–100° the high-vacuum distillate consistently exhibits a ratio of 2 ends/middle by n.m.r. Although lack of n.m.r. fine structure (other than some "hash" at extremely high resolution due to hydrogen–phosphorus coupling) eliminated this source of structure information, the unchanging ratio of ends to middles over a 20° temperature range indicates that reasonably pure decamethyltripolyphosphorylamide can be obtained by molecular distillation. As the temperature is raised above 100°, the relative amount of middle groups in the distillate is found to increase, so that at 130° the ratio of ends to middles in the distillate is unity. There is also a small amount of some orthophosphate in the 130° fraction, an n.m.r. finding which demonstrates that the rate of reorganization becomes comparable to the rate of molecular distillation at that temperature.

The Trimeric Ring Compound.—The crystalline trimeta compound (hexamethyltrimetaphosphorylamide) has been prepared according to the method used by Michaelis[7] in making its ethyl analog. We have confirmed the proximate analysis and find a slightly low molecular weight from the freezing point of benzene (307 found, 321 calcd.) as did Michaelis. When the crystals were dissolved in carbon tetrachloride, they exhibited only the single, sharp n.m.r. peak corresponding to middle groups. This information plus the pronounced build-up of trimetaphosphate on partial hydrolysis followed by paper chromatography demonstrates that Michaelis' formulation of this type of compound as a trimeric metaphosphoryldialkylamide is correct. The X-ray powder pattern of this ring trimer is given in Table I. Its melting point is +99.5°.

When concentrated (*ca.* 30%) solutions of the high-molecular-weight reorganization-equilibrium mixtures exhibiting R values near unity are prepared in carbon tetrachloride by heating at 100° for several hours, they start depositing crystals of the trimeta compound after standing for a day at room temperature. The crystals continue to form for a period of 2 weeks. On the other hand, when dissolution is effected by heating for only 5 minutes at 100°, no crystals appear upon standing for 2 weeks at room temperature. In view of the light-scattering measurements reported in the previous section of this paper, these results are to be interpreted in terms of a reorganization in hot carbon tetrachloride of long chains (with or without a small amount of branching) to rings and much shorter chains. Since the trimeta ring compound exhibits a moderately low solubility in carbon tetrachloride—with the solubility, perhaps, even being reduced by the presence of chain compounds, crystals are found to form.

TABLE I

OBSERVED X-RAY POWDER PATTERN OF HEXAMETHYLTRIMETAPHOSPHORYLAMIDE

d-Spacing (*A*)	Intensity	d-Spacing (*A*)	Intensity
11.9	vw	3.23	w
9.02	m	3.12	m
6.91	m	2.96	w
6.41	vst	2.79	w
6.06	st	2.70	w
4.48	m	2.55	m
4.27	m	2.30	w
4.11	st	2.21	w
3.45	m	2.00	m

Hydrolysis Data.—By hydrolyzing at 60° and *p*H 1 for increasing lengths of time, it is found that the amount of trimetaphosphate anion from its pure phosphoryldimethylamide analog and the amount of pyrophosphate anion from its pure analog reach maxima of more than 75% of the total phosphorus. In the case of the pure tripoly structure, this maximum corresponds to only 50% of the total phosphorus; and obviously, there is 100% conversion in the case of the ortho compound (hexamethylphosphorylamide.) Furthermore, reorganization equilibrium mixtures for which R is near unity give three quarters of the total phosphorus not moving from the origin at the time when hydrolysis had proceeded to the point where no more than several per cent. of the total phosphorus was moving with the solvent front in the form of unionized species. The conclusion from this work is that, in the polyphosphoryldimethylamides, the rate of acidic hydrolysis of P–N bonds is faster than the rate of hydrolytic scission of P–O–P linkages under the same acid or neutral conditions.

Discussion and Conclusions

Reorganization.—It is apparent from the data given above that the system obtained by mixing hexamethylphosphorylamide with phosphorus pentoxide corresponds to the modern theory of structural reorganization as developed in our Laboratory[13] and is inconsistent with the classical ortho-pyro-meta-oxide theory.[5] Further experimental work is needed to demonstrate whether or not the sorting of structural building units between molecules closely approximates a completely random process.[13]

Although the polyphosphoryldimethylamides are not ionized, they follow the Anti-branching Rule[19]

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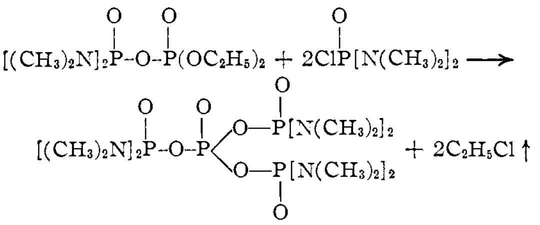
(19) See pp. 437–441, 706, 752, 761 and 768 of ref. 13.

quite closely. This means that factors other than charge difference between building units can play an important role in determining the values of the structural-unit-reorganization equilibria. As will be indicated in the discussion of Paper XI in this series, change in the degree of π-bonding when going from one building unit to another[20] may well be the cause of $K_1 = 5 \times 10^{-4}$ and $K_2 = 2.5 \times 10^{-2}$ instead of $K_1 = K_2 = 0.333$.

In this system, branches are not present in appreciable amounts until $R < 1.2$. This means that the region corresponding to $1.2 < R < 1.4$ is free of branches and of the ortho species so that all of the phosphorus must be present only in the form of chain and ring compounds. The highest average chain length in this region is $\bar{n} = 10 \pm 1$, with rings disregarded. For higher average chain lengths, the amount of chain branching and cross linking due to the presence of branch structural units must increase gradually.

Structures from Reaction Data.—Previous descriptions in the literature[8] of the tripoly, tetrapoly and isotetrapoly molecules are in error in that they refer to the reorganization-equilibrium mixtures and not to pure species as alleged. This is most obvious in the case of the isotetrapoly structure which Tolkmith believed was formed in the reaction



$$[(CH_3)_2N]_2\overset{O}{\overset{|}{P}}\text{-}O\text{-}\overset{O}{\overset{|}{P}}(OC_2H_5)_2 + 2Cl\overset{O}{\overset{|}{P}}[N(CH_3)_2]_2 \longrightarrow [(CH_3)_2N]_2\overset{O}{\overset{|}{P}}\text{-}O\text{-}\overset{O}{\overset{|}{P}}\left(O\text{—}\overset{O}{\overset{|}{P}}[N(CH_3)_2]_2\right)_2 + 2C_2H_5Cl\uparrow \quad (6)$$

If the reaction proceeded as written, 75% of the phosphorus would have been present as end groups and 25% as branches. Instead, n.m.r. showed that the reaction product consists of the reorganization-equilibrium mixture of 1% ortho, 48% ends and 51% middles with no branches being observed, when the reaction was carried out exactly as reported.[8] This is an example of the fact that reorganization often occurs during a reaction and that structure proofs acceptable in organic chemistry generally do not apply to inorganic chemistry or to the organic derivatives of elements in the second row or below in the Periodic Table!

Although use of hydrolysis to investigate inorganic structures often leads to false conclusions,[5] the predominately unbranched polyphosphoryldimethylamides appear to represent the unusual case in which the structure of the reaction products of hydrolysis carried out under optimum conditions can be related approximately to the structure of the unhydrolyzed substance. In other words, the data indicate that all dimethylamido groups can be converted to dimethylammonium ions of the corresponding phosphates without rearrangements involving the P–O–P linkages, when branching groups are absent or present in only small amounts. This is probably attributable to a combination of a slow rate of P–N scission with a considerably slower rate of P–O–P scission in water at room temperature or below.

The reorganization in carbon tetrachloride to form rings without concomitant molecular degradation indicates that rings are favored when the reorganizing molecules are separated by molecules of an inert solvent. This is in accord with the theory of ring formation developed by organic chemists. It, therefore, appears that the production of rings during the hydrolysis of long-chain phosphates is a phenomenon which is separable from the degradation process. In other words, the first step in path 3 in the hydrolysis scheme presented by McCullough, Van Wazer and Griffith[17] is probably a simple structural reorganization step not involving reaction with the water molecules.

Acknowledgment.—We wish to thank Dr. L. C. D. Groenweghe for equations 4 and 5 of this paper and the ideas underlying them.

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[20] J. R. Van Wazer, THIS JOURNAL, **78**, 5709 (1956). Also see H. H. Jaffé, *J. Inorg. Nuclear Chem.*, **4**, 372 (1957).

[CONTRIBUTION FROM THE W. A. NOYES LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS]

Transition Metal Ion Complexes of Dimethyl Sulfoxide

BY DEVON W. MEEK, DAREL K. STRAUB AND RUSSELL S. DRAGO[1]

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The preparation and characterization of transition metal ion complexes of dimethylsulfoxide have been described. The complexes have the general formula $[M[OS(CH_3)_2]_n][MX_4]$, where n = 4 or 6 and X is a halogen. Shifts of the infrared stretching frequency of the S–O bond in the direction of lower energy have been attributed to coördination through the oxygen. Using dimethylsulfoxide as the solvent and cobalt(II) as the metallic ion, it appears that chloride is more, and iodide less, strongly coördinated than the sulfoxide. Equilibria existing in solution are discussed.

Introduction

In the course of our research program in the area of nonaqueous solvents we have observed that several inorganic salts have appreciable solubility in dimethylsulfoxide (DMSO). Precipitation of some of these materials from the solvent is often accompanied by dramatic color changes leading one to suspect coördination by sulfoxide.

Very little has been reported on the ability of dimethylsulfoxide to coördinate. Carbonyl complexes of the type $Mo(CO)_3(DMSO)_3$[2] and [Fe-

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[1] Author to whom correspondence regarding this article should be addressed.

[2] W. Hieber, K. Englert and K. Rieger, *Z. anorg. allg. Chem.*, **300**, 295 (1959).