and

$$C_2 = -\theta_2 = -\frac{1}{2} + \frac{B_2p}{kT}$$

$$\theta_3 = \frac{1}{3} - \frac{B_2p}{kT} + \left(2B_2^2 - \frac{B_3}{2}\right)\left(\frac{p}{kT}\right)^2 \quad (97)$$

$$C_3 = \frac{1}{3} - \frac{2B_2p}{kT} + B_3\left(\frac{p}{kT}\right)^2$$

Pressure and temperature derivatives of these coefficients follow immediately. It is easy to show that the expression

$$\ln \frac{p}{p - \pi} = -\frac{\mu'_1}{kT} \quad (98)$$

for the osmotic pressure (using eq. 15 and 97) is equivalent to

$$\frac{p}{kT} = \rho_1 + \frac{\pi}{kT}$$

$$(99)$$

$$\frac{\pi}{kT} = \rho_2 + B_2\rho_2^2 + B_3\rho_3^2 + \ldots$$

as would be anticipated from the model.

Inert, Incompressible Solvent.—The solvent in this model is an inert incompressible fluid of volume $V_0 = N_1v_1$ whose only role is to provide a suspension medium for solute molecules. The solute molecules interact with each other, as in the previous model. The solution, as well as the pure solvent, is assumed incompressible with volume

$$V = V_0 + N_2v_2$$

For the pure solvent we write

$$Q(N_1,0,V) = Q_0\delta(V - V_0)$$

where $\delta(V - V_0)$ is the Dirac δ-function (introduced because of incompressibility). In general

$$Q(N_1,N,V) = \frac{Q_0\delta[V - (V_0 + Nv_2)]Z_N(V)}{N!\,\Lambda_2^{3N}} \quad (100)$$

where $Z_N(V)$ is given by eq. 95. Then, from eq. 2

$$\Delta_N = \frac{e^{-p(V_0 + Nv_2)/kT}\, Q_0Z_N(V_0 + Nv_2)}{N!\,\Lambda_2^{3N}} \quad (101)$$

and

$$e^{-\Delta F_N/kT} = \frac{Z_N(V_0 + Nv_2)}{N!\,(V_0 + v_2)^N} \quad (102)$$

For example, to terms in N_1^{-2}

$$e^{-\Delta F_2/kT} = \frac{1}{2}\left[1 + 2\frac{v_2}{V_0} - 2\frac{B_2}{V_0} - \left(\frac{v_2}{V_0}\right)^2 + \ldots\right]$$

$$(103)$$

$$e^{-\Delta F_3/kT} = \frac{1}{6}\left[1 + 6\frac{v_2}{V_0} - 6\frac{B_2}{V_0} + 6\left(\frac{v_2}{V_0}\right)^2 + 12\left(\frac{B_2}{V_0}\right)^2 - 18\frac{v_2B_2}{V_0^2} - 3\frac{B_3}{V_0^2} + \ldots\right]$$

and

$$\theta_2 = \frac{v_2}{v_1} - \frac{B_2}{v_1} = -C_2$$

$$\theta_3 = \frac{3}{2}\left(\frac{v_2}{v_1}\right)^2 + 2\left(\frac{B_2}{v_1}\right)^2 - 3\frac{v_2B_2}{v_1^2} - \frac{1}{2}\frac{B_3}{v_1^2} \quad (104)$$

$$C_3 = \left(\frac{v_2}{v_1}\right)^2 - 2\left(\frac{v_2B_2}{v_1^2}\right) + \frac{B_3}{v_1^2}$$

The pressure derivatives of these coefficients vanish, of course. The osmotic pressure is given by (with eq. 15)

$$\frac{\pi v_1}{kT} = -\frac{\mu'_1}{kT} \quad (105)$$

which can be shown without difficulty to be equivalent to

$$\frac{\pi}{kT} = \rho_2 + B_2\rho_2^2 + B_3\rho_2^3 + \ldots \quad (106)$$

BETHESDA, MD.

[CONTRIBUTION FROM MONSANTO CHEMICAL COMPANY, INORGANIC CHEMICALS DIVISION]

Structure and Properties of the Condensed Phosphates. XII. Reorganization Theory and Some Applications

BY J. R. PARKS AND J. R. VAN WAZER

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Reorganization is first treated in terms of equilibria between the various phosphate building units (branches, middles and ends) as well as between them and orthophosphate and unreacted M_2O. Variation of the relative proportions of these units with the M_2O/P_2O_5 mole ratio is discussed in terms of the amount of ionization of the M's in the M_2O–P_2O_5 system. Molecular structures are developed on the basis of statistics. In addition to the random-reorganization distribution function first obtained by Flory, a new distribution function is derived on the basis of Information Theory. The Flory distribution corresponds to flexible chains (un-ionized molecules); whereas the new distribution corresponds to rigid rods (polyelectrolytes). Both of these distribution functions apply only to those values of the M_2O/P_2O_5 ratio at which there is a vanishingly small amount of branching units. The principles presented herein are generally applicable to all systems composed of reorganizing molecular structures, ranging from un-ionized, non-polar molecules to completely ionized polyelectrolytes.

In a previous paper[1] the basic principles of the structure of sodium phosphate glasses were enunciated, and the key difference between these glasses and the condensed phosphoric acids was denoted in a qualitative manner. In the following discussion, we shall extend these principles quantitatively to all amorphous phosphates which are in equilibrium with respect to reorganization of their structures. It should be noted that the distribution theory derived here is of general application to all reorganizing systems—not only phosphates but other systems as well.

Reorganization Theory

Let M stand for an equivalent of any cation or organic radical in a phosphate, which can then be written as $xM_2O \cdot yP_2O_5$. The reorganizing, single-phase (liquid) phosphates can be described in terms of an M_2O/P_2O_5 mole ratio, $R = x/y$. Although in high-temperature melts the oxygens of a given

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[1] J. R. Van Wazer, THIS JOURNAL, **72**, 644 (1950).

PO_4 group undoubtedly change positions with each other and with neighboring PO_4 groups, it is reasonable to expect that the phosphorus atoms are quite universally surrounded by four oxygen atoms and that, at any instant, a certain number of the oxygen atoms are shared between PO_4 groups as demanded[1] by the M_2O/P_2O_5 mole ratio. This means that the configuration of the phosphorus and oxygen atoms at any instant can be discussed in terms of the usual elementary structural units: (1) isolated PO_4 units (orthophosphate), **o**; (2) end units, **e**; (3) middle units, **m**; and (4) triple branching units, b.[2]

As was done previously[3] in this series, the structural units will be considered as including the accompanying M atoms, or radicals, regardless of whether the M is covalently bonded to the oxygen or is completely ionized.

It is assumed that the molecules or molecule-ions of condensed phosphates interchange parts during the reorganization process by the making and breaking of P–O–P linkages. The first problem to be solved is to find the relative proportion of elementary structure units for any given value of R. Then, by using probability considerations, the structural units can be fitted together on a statistical basis into molecules or molecule-ions of various sizes and types. In addition to the phosphate elementary structural units, unreacted M_2O, **u**, must also be considered.

Exchange between Structural Units.—Branching, middle and end units can react with each other or with orthophosphate and unreacted M_2O so as to form different structural units. All of the combinations whereby b, **m**, **e**, o, and **u** can interchange roles with each other are given by the equations[4]

$$2\mathrm{m} = \mathrm{b} + \mathrm{e} \qquad (1)$$

$$2\mathrm{e} = \mathrm{m} + \mathrm{o} \qquad (2)$$

$$2\mathrm{o} = 2\mathrm{e} + \mathrm{u} \qquad (3)$$

The three equations given above represent equilibria, and it is natural to think of them in terms of equilibrium constants. Such equilibrium constants, however, are rather unusual in that the quantities **b**, **m** and **e** represent parts of molecules or molecule-ions rather than the whole molecule or ion. However, we assume equilibrium between these structural units and, therefore, presuppose that the molecules or molecule-ions make and break many times during the period in which equilibrium is achieved. This means that, for the purposes of this discussion, the molecular structures may be considered as unstable agglomerates, having no more effect on the equilibria than, say, the association of water molecules has on equilibria involving H_2O. The one objection to this idea is found in equation 3 in which **u** appears. This unreacted M_2O should also break apart, and equations might be given for this process. To avoid such a complication and the alternative one in which a large number of molecular equations, such as the conversion of tripolyphosphate into ortho- plus pyrophosphate, would be used, equation 3 can be treated as either an equilibrium between molecular parts (o, **e** and **u**) or an equilibrium between the molecules and/or ions themselves (o, 2e and **u**). Since the best approximation ought to be found with a transition from the molecular equilibrium (K_3', below) at $R >$ *ca.* 4 to the structural-unit equilibrium (K_3, below) at $R \leqslant$ *ca.* 2, both K_3' and K_3 will be compared with the physical data; and the one giving the best fit will be used with the other two equilibrium constants, all of which are shown below.

$$K_1 = \frac{be}{m^2} \qquad (4)$$

$$K_2 = \frac{mo}{e^2} \qquad (5)$$

$$K_3 = \frac{e^2u}{o^2} \text{ or } K_3' = \frac{(2e)u}{o^2} \qquad (6)$$

In addition to equations 4, 5 and 6 there is another equation, 7, defining R in terms of the structural units and also a normalizing equation, 8

$$R = M_2O/P_2O_5 = M/P = \frac{3o + 2e + m + 2u}{b + m + e + o} \qquad (7)$$

$$b + m + e + o + u = 1 \qquad (8)$$

In the five equations—4, 5, 6, 7 and 8—there are five unknowns and three adjustable parameters (K_1, K_2 and K_3 or K_3') plus the composition parameter R. Thus, knowing K_1, K_2 and K_3, a solution can be obtained for the relative proportions of phosphate structural units as a function of R. Numerical values have been calculated by Professor Churchill of Antioch College by putting the five equations in parametric form.[5] Solution of these five equations shows that, for any set of values for the equilibrium constants, b reaches a maximum value of 100% of the total phosphorus at $R = 0$ and m, e and o reach their maximum values at $R = 1$, 2 and 3, respectively.

A priori reasoning leads to the conclusion that

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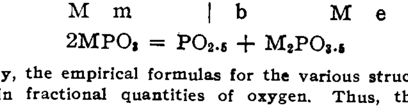
[2] When such elements as aluminum and boron are present in the phosphates, it is also possible to have a quadruple branching unit, which is a PO_4 group in which all four oxygen atoms are covalently bonded to neighboring PO_4 and/or, say, AlO_4 groups through sharing of oxygen atoms. This structural unit is ignored in this discussion although it could be included for the sake of completeness. It will be obvious, as the discussion proceeds, as to what modifications should be made to the theory to include such a quadruple branching unit in the structure.

[3] J. R. Van Wazer and E. J. Griffith, THIS JOURNAL, **77**, 6140 (1955).

[4] Equations 1, 2 and 3 can also be written in terms of PO_4 groups or in terms of the empirical composition of the structural units involved, as shown below for equation 1.



$$2\ \text{-O-}\underset{\underset{\mathrm{M}\ \ \mathrm{m}}{\mathrm{O}}}{\overset{\mathrm{O}}{\mathrm{P}}}\text{-O-} = \text{-O-}\underset{\underset{|\ \ \mathrm{b}}{\mathrm{O}}}{\overset{\mathrm{O}}{\mathrm{P}}}\text{-O-} + \text{-O-}\underset{\underset{\mathrm{M}\ \ \mathrm{e}}{\mathrm{O}}}{\overset{\mathrm{O}}{\mathrm{P}}}\text{-OM}$$

$$2MPO_3 = PO_{2.5} + M_2PO_{3.5}$$

Obviously, the empirical formulas for the various structural units will contain fractional quantities of oxygen. Thus, the reaction whereby two end groups come together to form the pyrophosphate is given by the empirical formulas as

$$2M_2PO_{3.5} \longrightarrow M_4P_2O_7$$

[5] Material supplementary to this article has been deposited as Document number 5165 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 \$2.50 for photoprints or \$1.75 for 35 mm. microfilm, in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

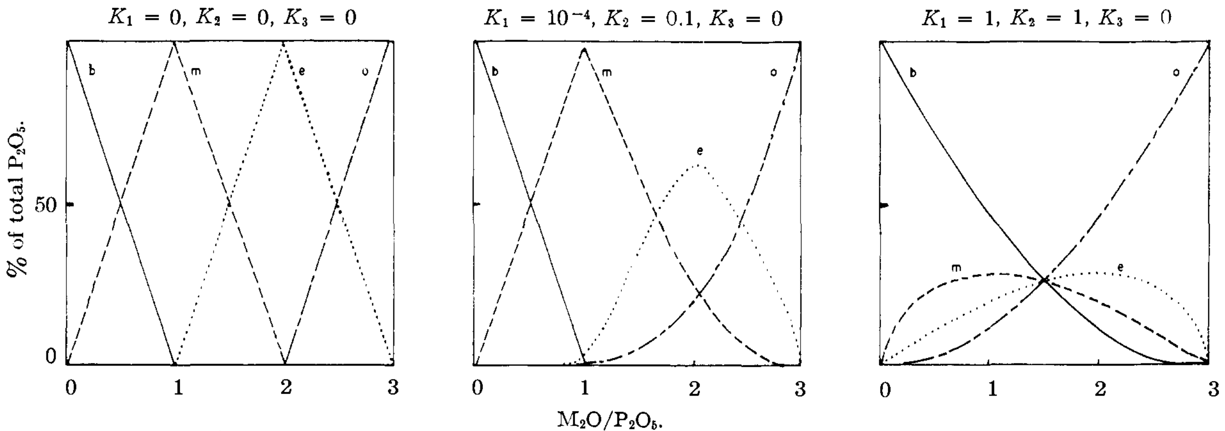


Fig. 1.—Distribution of branches, middles, ends and ortho for various values of the equilibrium constants K_1 and K_2. The completely ionized case is represented by $K_1 = K_2 = K_3 = 0$ and the completely un-ionized case by $K_1 = K_2 = 1$ with $K_3 = 0$.

the values of K_1 and K_2 are very dependent on whether the M is ionized or covalently bonded to the oxygen. In the case of complete ionization of the M (no M–O bonds), the orthophosphate ions, ends, middles and branching units correspond to PO_4 groups bearing 3, 2, 1 and 0 negative charges, respectively. This means that driving equations 1 and 2 to the right converts two PO_4 groups having given charges into a group having a higher and a group having a lower charge, so that there would be high and low local concentrations of the counter ions, M^+. As previously stated,[1] such local concentrations of counterions are highly improbable, with the over-all equilibrium in the ionic case corresponding to equation 1 and 2 being strongly driven to the left, so that $K_1 \rightarrow 0$ and $K_2 \rightarrow 0$.

For the completely non-ionic case, one would expect $K_1 = 1$ and $K_2 = 1$, if there were no weighting of the probabilities of occurrence of **b**, m and **e** units. However, the Antibranching Rule[1,3,6] should cause $K_1 \rightarrow 0$, possibly even for un-ionized phosphates such as esters.

The question of whether there is any unreacted or free M_2O depends on the relative free energies of the unreacted M_2O and the phosphate, $xM_2O \cdot yP_2O_5$. Generally speaking, equation 3 will be shifted completely to the left except for those cases where M_2O is an extremely stable compound in itself. Where M_2O stands for metal oxides, K_3 or K_3' will probably either be 0 or very small; whereas in the case where M stands for an alkyl or aryl radical, K_3 probably will be relatively large. For the phosphoric acids—where M stands for H—it is also expected that K_3 or K_3' also should be appreciably large, ranging from, say, 10^6 to 10^2. The effect of going from a completely ionized M to an M held in the phosphate structure by strong covalent M–O bonds is shown in Fig. 1 in which it is assumed arbitrarily that there is no unreacted M_2O in either limiting case.

Size-distribution Functions.—The concept of the presence, in a reorganizing liquid or melt, of various proportions of structural units in equilibrium with each other (as outlined in the previous section of this paper) leads naturally to the use of probability notions in obtaining the equations previously derived by Flory[7] and in obtaining a new distribution function. It is interesting to note that our derivation of the Flory distribution functions, which is given in the supplementary discussion,[5] is not based on a kinetic mechanism or the use of the Boltzman H-Theorem.[7] The statistical calculations indicate that infinitely or macro-branched, wall-to-wall structures are to be found only in the composition range

$$0 \leqslant R < \frac{3o + 2e + m + 2u}{2.21e + m + o}, \text{ for } b > 0 \quad (9)$$

In the range of R given above (where there is an infinite network stretching from wall to wall), there will be also, in the general case, some chain and ring structures as well as orthophosphate and unreacted M_2O. The weight fraction of the total phosphorus that is contained in these lower-molecular weight constituents is given by w. Obviously the weight fraction of the total phosphorus occurring in the branched infinite structure is equal to $1 - w$.

$$w = \frac{(1 - o - u)e^2}{(1 - u)(2b + e)^2} + \frac{o}{1 - u} \quad (10)$$

In the general case, where orthophosphate and unreacted M_2O may be present, equation 4 in the previous paper[1] on this subject takes the following form in which n is the number of phosphorus atoms per chain and $\bar{n}$ is the number-average number of phosphorus atoms per chain. This equation applies only to those values of R where b is vanishingly small. It predicts the size distribution of chain phosphates and ignores the possibilities of ring structures. No other type of condensed phosphate is possible because there are no branching units.

$$w(n) = \frac{n}{\bar{n}(\bar{n} - 1)} \left(\frac{\bar{n} - 2}{\bar{n} - 1}\right)^{\bar{n} - 2} \left(1 - \frac{o}{1 - u}\right) \quad (11)$$

$$\text{for } b = 0;\ n = 2, 3, 4, —, \infty;\ \text{and } \bar{n} \geqslant 2$$

Equation 11, which is an extension of Flory's random reorganization distribution was derived by making no assumptions as to the configuration of

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(6) J. R. Van Wazer, This Journal, **78**, 5709 (1956).

(7) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953; This Journal, **64**, 2205 (1942).

the chains, the size distribution of which it describes. This is equivalent to assuming that every possible configuration can be assumed by the chain structures, or, in other words, that the chains are infinitely flexible. Therefore, equation 11 ought to apply to non-ionic or only partially ionized molecular species existing in those regions of R where b is vanishingly small.

In the extreme ionic case where the counterions are completely dissociated from the phosphate molecule-ions, it is to be expected that the chain phosphates, occurring for values of R at which b is vanishingly small, would approximate rigid rods. This means that the reorganizing phosphate can be considered as a "brush heap" of rod-like molecule ions so arranged that there is equal probability of finding equal numbers of any given sized molecule-ion oriented in any direction. By the use of Information Theory, as described in the supplementary discussion,[5] the following distribution function is obtained. As previously pointed out, there should be no orthophosphate or unreacted M_2O as well as no branching units in the completely ionic case for $1 < R \leqslant 2$, which is the composition range for the completely ionic case to which the equation applies

$$w(n) = \frac{-4B \log_2 m}{\sqrt{\pi} A^3 \bar{n}} \int_{n-1/2}^{n+1/2} n[\log_2 e + (n-2)\log_2 m]^2 \exp\left\{-\frac{[\log_2 e + (n-2)\log_2 m]^2}{A^2}\right\} dn \text{ for } n \geqslant 2; \text{ and where } m = \frac{\bar{n}-2}{\bar{n}-1} \text{ and } e = \frac{1}{\bar{n}-1} \quad (12)$$

In this equation, the constant B is a normalizing factor and A is proportional to the standard deviation of the distribution function, which in turn is proportional to the square root of the mean square logarithm of the probabilities of the molecules comprising the population of molecule-ions. The characteristic constants of this function can be determined by demanding that they simultaneously satisfy the equations

$$\frac{4B}{\sqrt{\pi A^3}} \int_2^\infty I^2 \exp\left[-\frac{I^2}{A^2}\right] \mathrm{d}n = 1 \quad (13)$$

and

$$\frac{4B}{\sqrt{\pi A^3}} \int_2^\infty nI^2 \exp\left[-\frac{I^2}{A^2}\right] \mathrm{d}n = \bar{n} \quad (14)$$

where

$$I = -[\log_2 e - (n-2)\log_2 m] \quad (15)$$

Comparison with Experiment

Through the application of paper chromatography some reasonably accurate size-distribution studies on phosphates have been carried out[8-10] by Westman and associates at the Ontario Research Foundation. The experimental data[11] are compared with the theoretically calculated values for (1) the distribution of phosphate structural units as a function of the M_2O/P_2O_5 mole ratio and (2) one or the other of the size-distribution functions presented in equations 11 and 12.

Exchange between Structural Units.—In Fig. 2, the relative proportions of b, m, e, o and u are plotted as a function of R for the condensed phosphoric acids. The curves shown in this figure were calculated on the assumption that $K_1 = 1.0 \times 10^{-3}$, $K_2 = 8 \times 10^{-2}$ and $K_3' = 2.0 \times 10^{-2}$ on a mole-fraction basis. The experimental data,[9] presented as individual points, agree with the theoretically derived curves. Although the experimental data only covered the range from $R = 1.2$ to $R = 3.6$, a reasonably good estimate could be made of the shape of the curves from $R = 0$ to $R = 1.2$ by extrapolating the line corresponding to middle groups to the value of $R = 1.00$, where the intercept is equal to 95% of the total P_2O_5 as m. It is from this value that $K_1 = 10^{-3}$ was obtained. The values of K_3 and K_3' were calculated, point by point, from the experimental data. When the results of these calculations were plotted, it was found that K_3' varied by less than a factor of 10 throughout the experimentally important range of $R = 2.6$ to $R = 3.3$, whereas K_3 varied by a factor of 10^3 over the same range.

The data shown in Fig. 2 agree very well with the picture presented for an un-ionized phosphate obeying the Antibranching Rule. They also indicate that the H–O bond in the condensed phosphoric acids have approximately the same character as the H–O bond in water.

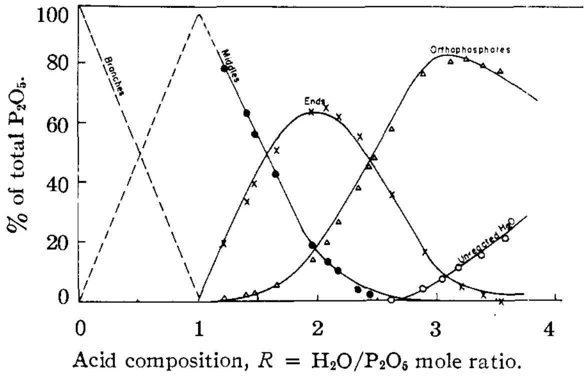

Fig. 2.—Relative proportions of branching, middle and end units as well as orthophosphate and free water as a function of the H_2O/P_2O_5 mole ratio. The smooth curves were calculated on the assumption of $K_1 = 10^{-3}$; $K_2 = 0.08$ and $K_3' = 0.02$.

The experimental data on the sodium acid phosphates[10] for which the Na/H mole ratio equals unity were not very self-consistent; therefore, before these data were compared with theory, they were smoothed, then normalized for all values of R, and finally resmoothed. This process was a purely empirical operation, based on the principles that (1) the curves showing the variation of the amount of a particular species as a function of R must be continuous and (2) the sum of the $Na_2O + H_2O$ corresponding to all of the various molecular species present for a given value of R divided by

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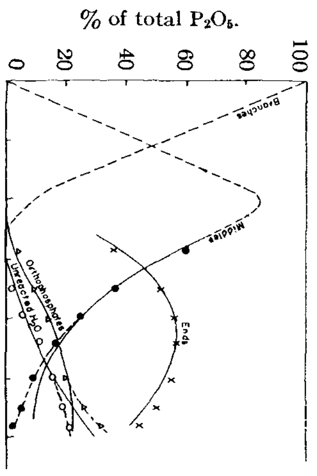
(8) A. E. R. Westman and J. Crowther, *J. Am. Ceramic Soc.*, **37**, 420 (1954); also see A. E. R. Westman and P. A. Gartaganis, *ibid.*, in press.

(9) A. L. Huhti and P. A. Gartaganis, *Can. J. Chem.*, **34**, 785 (1956). Also private commun. from Prof. S. Ohashi of Kanayawa Univ., Japan.

(10) Private commun. from A. E. R. Westman and P. A. Gartaganis. These investigators have found a possible source of error in their preparation of the sodium acid phosphates and are re-investigating the system before publishing their work.

(11) Also see H. Grunze, *Silikattechnik*, **7**, 134 (1956).

the sum of the P_2O_5 corresponding to these species must necessarily equal R. In spite of the fact that these data were smoothed, the correlation between theory and experiment (when the relative proportions b, m, e, o and u were plotted as a function of R) was not extremely good, as is shown in Fig. 3. Again, a value of K_1 equal to 10^{-2} was chosen from the intercept of the m curve with the line corresponding to R = 1.00, whereas K_2 = 1.0×10^{-1} and K_3 = 1.0 were obtained by putting the experimental values into the appropriate equations. In this case, it was found that K_3' varied much more than K_3 so the latter was used.



Composition, R = $(Na_2O + H_2O)/P_2O_5$ mole ratio.

Fig. 3.—Relative proportions of branching, middle and end units as well as orthophosphate and free water as a function of the $(Na_2O + H_2O)/P_2O_5$ mole ratio for Na_2O = H_2O. The smooth curves are calculated on the assumption that K = 0.01, K_2 = 0.10 and K_3 = 1.00.

In the case of the sodium phosphate glasses, which have been studied only between R = 1 and R = 1.7, it is found[12] that there is no orthophosphate and that there are no branching points, except for a small amount,[13] about 0.1% of the total P_2O_5, at values only slightly larger than R = 1.00. These results are in accord with the distribution to be expected for the completely ionic case (K_1 = K_2 = K_3 = 0) as shown in the first graph of Fig. 1.

Size-distribution Functions.—A comparison of theory and experiment is given in Tables I, II and III for the condensed phosphoric acids, the amorphous sodium acid phosphates, and the vitreous sodium phosphates, respectively. In Tables I and II the theoretical size distributions were calculated on the basis of a flexible chain by the use of equation 11. On the other hand, the theoretical size distributions presented in Table III were calculated on the basis of the rigid-rod model, using equation 12.

It is instructive to compare the size-distribution curves for certain particular values of R. This has been done in Figs. 4 and 5 for a short-chain and a longer-chain, condensed phosphoric acid. It can be seen from these figures that the correspondence between theory and experiment is very good, especially in the case of the acid containing the shorter chain phosphates. If the rigid-rod model of the phosphate chain had been used instead

TABLE I: MOLECULAR COMPOSITION OF THE STRONG PHOSPHORIC ACIDS COMPARED WITH THE THEORETICAL COMPOSITION CALCULATED FROM THE FLEXIBLE-CHAIN MODEL

Anal.				Percentage of total P_2O_5 as																			
Wt. % P_2O_5	H_2O/P_2O_5 R	Over-all $\bar{n}$	$\bar{n}$ cor. for unreacted H_2O	Ortho		Pyro		Tripoly		Tetrapoly		Pentapoly		Hexapoly		Heptapoly		Octapoly		Nonapoly		Higher	
				Exper.	Theory	Exper.	Theory	Exper.	Theory	Exper.	Theory	Exper.	Theory	Exper.	Theory	Exper.	Theory	Exper.	Theory	Exper.	Theory	Exper.	Theory
69.0	3.544	0.786	1.003	99.48	...	0.52																	
70.0	3.381	0.837	1.013	97.4	...	2.6																	
71.0	3.222	0.900	1.029	94.2	...	5.8																	
72.0	3.068	0.967	1.056	89.4	...	10.6																	
73.0	2.918	1.043	1.102	81.5	...	18.5																	
75.0	2.630	1.227	1.260	60.2	...	35.4	36.7	4.4	3.9	..	0.4												
76.2	2.462	1.368	...	49.2	...	42.0	43.1	8.4	7.2	0.4	1.1	..	0.1										
77.1	2.344	1.488	...	38.5	...	46.8	50.6	12.2	9.5	2.5	1.6	..	0.6										
78.3	2.192	1.678	...	28.0	...	49.1	47.7	16.5	16.3	5.2	4.7	1.2	1.3										
79.2	2.069	1.871	...	20.5	...	46.2	46.7	20.6	20.5	8.8	8.0	3.4	2.9	0.5	1.0								
80.1	1.960	2.083	...	15.4	...	39.1	40.4	24.4	22.9	12.7	11.5	5.7	5.4	2.3	2.5	0.5	1.1	..	0.5				
83.0	1.620	3.226	...	5.6	...	18.7	18.3	17.8	17.5	14.7	14.8	12.0	11.8	8.6	9.0	7.2	6.7	5.1	4.9	2.5	3.5	7.8	7.9
84.3	1.470	4.255	...	3.2	...	9.9	9.4	10.8	10.7	11.3	10.7	10.4	10.1	8.8	9.1	8.3	8.0	8.5	6.9	6.8	5.9	22.0	26.0
84.9	1.400	5.000	...	2.3	...	6.0	5.9	7.1	7.2	9.2	7.8	8.5	7.9	7.4	7.6	8.3	7.2	8.4	6.7	7.1	6.1	35.9	41.3
85.5	1.333	6.000	...	1.7	...	3.6	3.8	4.7	4.8	7.0	5.5	6.0	5.8	6.0	6.0	6.9	5.9	7.1	5.8	6.6	5.5	50.4	55.2
86.0	1.286	7.000	...	1.5	...	2.8	3.1	3.6	4.0	6.0	4.6	5.7	5.0	5.7	5.2	5.8	5.3	5.5	5.2	5.2	5.1	58.4	61.0
86.3	1.250	8.000	...	1.4	...	2.3	2.4	2.8	3.1	4.4	3.7	4.4	4.1	4.9	4.3	3.5	4.5	4.9	4.5	4.3	5.4	67.1	67.5
86.6	1.222	9.000	...	1.3	...	1.8	2.2	2.4	2.9	4.2	3.4	4.1	3.8	4.3	4.0	4.5	4.2	4.5	4.3	4.0	4.3	68.9	69.7

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[12] J. R. Van Wazer, THIS JOURNAL, **72**, 647 (1950).

[13] 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); J. F. McCullough, J. R. Van Wazer and E. J. Griffith, *ibid.*, **78**, 4528 (1956).

TABLE II

MOLECULAR COMPOSITION OF SODIUM ACID PHOSPHATE GLASSES (Na_2O = H_2O) COMPARED WITH THE THEORETICAL COMPOSITION CALCULATED FROM THE FLEXIBLE-CHAIN MODEL

Anal. Wt. % P_2O_5	Anal. (Na_2O + (H_2O)/P_2O_5 R	Anal. Over-all $\bar{n}$	Anal. $\bar{n}$ cor. for unreacted H_2O	Percentage of total P_2O_5 as Ortho		Pyro		Tripoly		Tetrapoly		Pentapoly		Hexapoly		Heptapoly		Octapoly		Nonapoly		Higher	
				Exper.	Theory	Exper.	Theory	Exper.	Theory	Exper.	Theory	Exper.	Theory	Exper.	Theory	Exper.	Theory	Exper.	Theory	Exper.	Theory	Exper.	Theory
55.0	2.93	1.05	1.45	40.3	...	51.7	52.2	7.96	6.66	...	0.76												
56.0	2.79	1.12	1.54	34.4	...	52.5	52.9	11.5	10.4	1.61	1.83												
57.0	2.68	1.19	1.63	29 4	...	52.0	52.4	14.8	14.0	3.09	3.30	0.699	0.730	...	0.140								
58.0	2.57	1.27	1.72	25.6	...	50.2	50.6	17.8	16.9	4.66	5.01	1.79	1.39	...	0.370								
59.0	2.47	1.36	1.81	22.7	...	47.0	47.4	20.5	19.3	6.16	7.02	2.78	2.39	0.894	0.780								
60.0	2.37	1.46	1.89	20.8	...	43.7	44.3	22.3	20.8	7.60	8.69	3.80	3.40	1.80	1.28	...	0.47						
61.0	2.27	1.58	1.96	19.1	...	40.6	41.3	23.5	21.8	9.18	10.2	4.94	4.47	2.72	1.88								
62.0	2.18	1.70	2.05	17.7	...	37.4	38.2	24.1	22.3	10.6	11.5	5.99	5.61	3.65	2.62	0.711	1.19						
63.0	2.08	1.84	2.14	16.2	...	34.13	35.0	24.1	22.4	12.1	12.7	7.05	6.79	4.60	3.47	1.74	1.73	...	0.84				
64.0	2.00	2.01	2.24	14.9	...	31.0	31.9	23.6	22.2	13.3	13.7	7.97	7.94	5.52	4.41	2.76	2.39	0.920	1.26	...	0.66		
65.0	1.91	2.19	2.39	13.3	...	27.5	28.0	22.5	21.4	14.1	14.5	8.84	9.25	6.33	5.65	3.61	3.36	1.81	1.95	0.904	1.12	1.20	1.44
66.0	1.83	2.41	2.57	11.6	...	24.2	24.5	21.1	20.3	14.6	14.9	9.55	10.3	6.99	6.82	4.63	4.40	2.66	2.78	1.77	1.72	2.86	2.67
67.0	1.75	2.67	2.75	10.3	...	21.7	21.6	19.4	19.0	14.8	14.9	10.2	11.0	7.62	7.74	5.37	5.31	3.42	3.52	2.44	2.36	4.78	4.27
68.0	1.67	2.98	..	8.97	...	19.1	18.1	17.7	17.1	14.3	14.4	10.7	11.4	8.38	8.62	6.04	6.34	4.19	4.58	3.12	3.25	7.02	7.20
69.0	1.63	3.18	..	7.66	...	16.8	16.5	15.9	16.2	14.3	14.1	11.1	11.5	9.03	9.00	6.68	6.86	4.91	5.12	3.63	3.76	9.92	9.34
70.0	1.57	3.51	..	6.52	...	14.4	13.8	14.1	14.3	13.3	13.1	11.2	11.3	9.48	9.32	7.31	7.49	5.53	5.90	4.05	4.57	14.1	13.7
71.0	1.51	3.92	..	5.25	...	11.9	10.9	12.3	11.9	12.0	11.6	10.7	10.8	9.61	9.26	7.73	7.89	5.85	6.59	4.26	5.41	20.5	20.7
72.0	1.44	4.54	..	3.94	...	9.25	8.27	10.4	9.55	10.4	9.80	9.64	9.43	9.25	8.72	7.97	8.28	5.90	7.29	6.31	6.31	28.9	28.4

TABLE III

MOLECULAR COMPOSITION OF THE SODIUM PHOSPHATE GLASSES COMPARED WITH THE THEORETICAL COMPOSITION CALCULATED FROM THE RIGID ROD MODEL

Anal. Wt. % P_2O_5	Anal. Na_2O/P_2O_5 R	Anal. $\bar{n}$	Percentage of total P_2O_5 as Ortho		Pyro		Tripoly		Tetrapoly		Pentapoly		Hexapoly		Heptapoly		Octapoly		Monapoly		Higher	
			Exper.	Theory	Exper.	Theory	Exper.	Theory	Exper.	Theory	Exper.	Theory	Exper.	Theory	Exper.	Theory	Exper.	Theory	Exper.	Theory	Exper.	Theory
53.383	2.00000	2.0	0.00	0.00	100.0	100.0																
54.803	1.88888	2.25	.00	.00	91.81	...	8.19	...														
55.994	1.80000	2.5	.00	.00	72.24	...	27.76	...														
57.007	1.72727	2.75	.00	.00	47.03	28.94	52.13	55.34	0.84	14.84	...	0.86	...	0.02								
57.881	1.66667	3.0	.00	.00	24.32	21.0	48.55	44.1	20.41	27.2	5.11	6.7	1.61	0.8	...	0.2						
59.308	1.57143	3.5	.00	.00	11.13	13.73	38.27	26.83	28.11	28.26	13.12	18.91	5.52	8.63	2.33	2.83	1.02	0.67	0.48	0.11	...	0.03
60.426	1.50000	4.0	.00	.00	6.65	10.03	28.25	18.06	27.43	21.96	16.87	20.11	9.41	14.54	5.70	8.56	2.74	4.18	1.77	1.72	1.16	0.84
61.324	1.44444	4.5	.00	.00	4.74	7.74	22.17	13.15	23.99	16.81	17.30	17.51	11.52	15.46	8.24	11.85	4.60	7.99	3.15	4.77	4.29	4.72
62.063	1.40000	5.0	.00	.00	3.24	6.21	16.24	10.12	20.16	13.15	16.45	14.59	12.68	14.27	9.43	12.53	6.71	10.01	4.39	7.35	10.69	11.77
62.681	1.36364	5.5	.00	.00	2.65	5.06	13.94	8.09	19.14	10.57	17.92	12.14	14.12	12.56	8.92	11.95	6.40	10.51	4.76	8.67	12.15	20.45
63.205	1.33333	6.0	.00	.00	1.88	4.23	10.09	6.64	14.89	8 68	13.46	10.18	11.28	10.91	9.61	10.89	9.26	10.21	6.94	9.07	22.58	29.19
63.655	1.30769	6.5	.00	.00	1.81	3.62	8.71	5.57	13.07	7.28	12.32	8.63	11.70	9.45	11.12	9.75	9.11	9.52	6.32	8.88	25.84	37.30
64.389	1.26667	7.5	.00	.00	1.24	2.69	6.38	4.08	9.44	5.37	9.09	6.43	10.74	7.24	9.91	7.76	8.53	7.96	7.74	7.89	36.92	50.58
65.204	1.22222	9.0	.00	.00	0.95	1.89	4.35	2.81	7.63	3.64	6.52	4.44	9.74	5.08	8.00	5.60	7.49	5.97	6.13	6.18	49.19	64.39

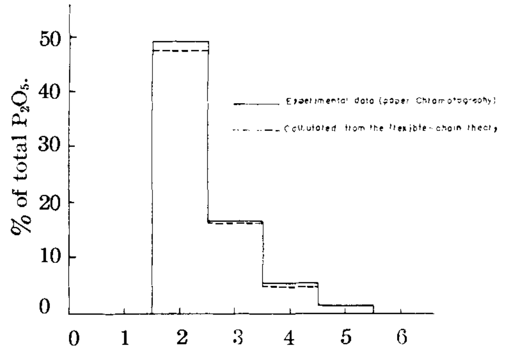

Fig. 4.—Size-distribution of chain phosphate in a condensed phosphoric acid for which R = 2.192, corresponding to 78.3% P_2O_5.

of the flexible-chain model, the theory would have agreed very poorly with experiment. Thus, for the condensed phosphoric acid of low molecular weight described in Fig. 4, the rigid-rod model would give a considerably lower value for the pyrophosphate (n = 2) and would peak at the tripolyphosphate anion (n = 3). This model also would give moderately high proportions of molecular species corresponding to n = 5, 6, 7 and 8. For the condensed phosphoric acid described in Fig. 5, the distribution curve for the rigid-rod model would exhibit only a very flat maximum at a lower value of the per cent. of the total P_2O_5, with this maximum occurring around n = 3.

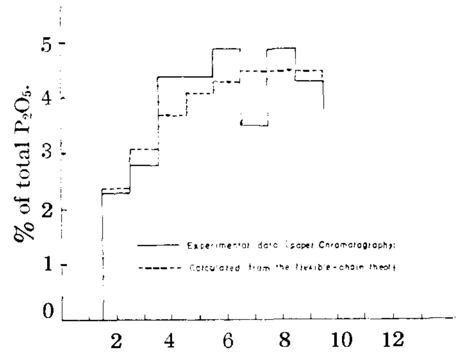

Fig. 5.—Size-distribution of chain phosphates in a condensed phosphoric acid for which R = 1.286, corresponding to 86.0% P_2O_5.

In the case of the sodium acid phosphate glasses for which Na/H = 1, it is again found that the flexible-chain model satisfies the experimental data. Thus, in a sodium–hydrogen phosphate in which, on the average, the sodium ions (assumed to be completely ionized) alternate with the hydrogen ions (assumed to be covalently bonded), the approximation of an infinitely flexible chain applies. Apparently, the alternation of negatively charged PO_4 groups with neutral ones allows the molecule-ion sufficient flexibility to assume essentially all of its possible configurations.

The size distributions of chain phosphates in sodium phosphate glasses for which n = 3.0 and 7.5 are shown in Fig. 6 and 7, respectively. Again, the agreement between experiment and theory is relatively good. As previously stated, the flexible-chain model does not fit at all for the low-molecular-weight sodium phosphate glasses. Thus, in Fig. 6, the maximum would appear at n = 2 instead of the observed value of n = 3. Likewise, in Fig. 7, the maximum would also occur at too low value, and the over-all distribution curve would be too sharp. Presumably, the fact that the theoretical rigid-rod distribution curve exhibits its maximum at n = 8 in Fig. 7 as compared to the experimental maximum at n = 6 is explained by saying that for the longer chains there should be a small amount of flexibility and that the rigid-rod model, although it gives a reasonably good fit, is not a perfect analogy of the real case. Another factor, which probably is more important, is that molecular volumes were ignored in the calculations. It appears that the deviations between theory and experiment in Figs. 5 and 7 may be due in great part to this volume error which should be most pronounced for intermediate chain lengths.

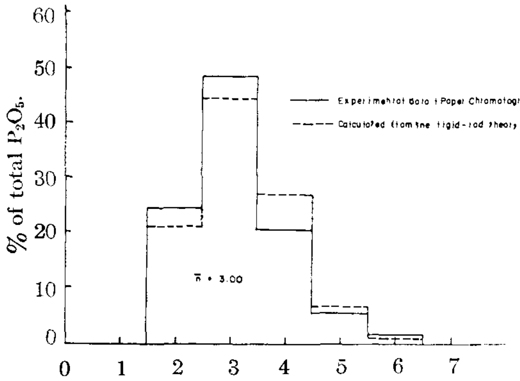

Fig. 6.—Size-distribution of chain phosphates in a sodium phosphate glass for which R = 1.67 corresponding to 57.88% P_2O_5.

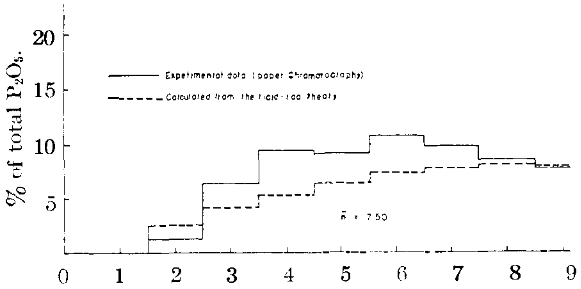

Fig. 7.—Size-distribution of chain phosphates in a sodium phosphate glass for which R = 1.27 corresponding to 64.37% P_2O_5.

Comparison of the rigid-rod and flexible-chain models with solubility fractionation data[12] on long-chain sodium phosphate glasses (20 < $\bar{n}$ < 200) indicates that the true state of affairs lies part way between the extremely flexible and extremely rigid case, since the experimental data are found to lie between the two distribution curves. This probably means that the long chains can show an appreciable amount of curvature even though they are made up of small segments of essentially straight rigid rods. In other words, the various configurations involving large arcs having small curvature are available to the long molecules, whereas highly "kinked" configurations are not.

Discussion

Glass Structure.—In order to arrive at a reorganization equilibrium in a reasonable length of time, it is probably necessary for the amorphous material to be fluid. This means that any discussion of vitreous phosphates in terms of reorganization equilibria must refer to the melt from which the glass was obtained. When the random-reorganization theory was brought to the attention[6,14] of glass technologists, some of the more reactionary adherents of the Zachariasen[15] theory questioned whether measurements on solutions were pertinent to the structure of the vitreous solid before it was dissolved. This reasoning would, of course, normally occur to a person well-versed in the technology of the silicate glasses and knowing very little about phosphate glasses having an M_2O/P_2O_5 mole ratio greater than unity, since silicates readily polymerize or depolymerize in aqueous solutions under conditions where the unbranched phosphates are stable. Proof that dissolution of a sodium phosphate glass for which $1.0 \leqslant R \leqslant 1.7$ is not accompanied by appreciable changes in the kind and relative proportions of the phosphate molecule-ions is afforded by the following data: (1) rapid or slow dissolution gives the same distribution and kind of molecule-ions. (2) Dissolving the glass in solutions of electrolytes (including sodium hydroxide) has no effect on the distribution. (3) The heat of dissolution of a sodium phosphate glass is of the same order of magnitude as the heat of dissolution of equivalent crystalline phosphates (9.9 kcal./mole of P_2O_5 for a $Na_2O-P_2O_5$ glass for which $\bar{n} = 4.6$ and 7.9 kcal./mole of P_2O_5 for a glass for which $\bar{n} =$ *ca.* 2.30, as compared to 12.0, 10.7, and 9.4 kcal./mole of P_2O_5 for $Na_4P_2O_7$, $Na_5P_3O_{10}$-I, and $Na_5P_3O_{10}$-II, respectively). (4) No orthophosphate is found in fresh solutions. (5) Solutions of sodium phosphate glasses for which $R \geqslant 1.0$ may be dehydrated readily *in vacuo* at room temperature to give a horny, glass-like material which, upon redissolution, is found to exhibit essentially the same molecular composition. The term "horny, glass-like material" was employed in the above sentence because the last few per cent. of water, which is difficult to remove on dehydration, acts as a plasticizer causing the resulting amorphous solid to be somewhat flexible and not nearly as brittle as the original glass. It should also be noted that crystalline chain and ring phosphates can be dissolved, recrystallized and redissolved without changing their anionic structures.

Even though silicates cannot be studied readily in aqueous solution as can phosphates, there seems to be no reason to doubt that the structure of silicate glasses is quite similar to that of phosphate glasses, with a quadruple branching point occurring in the silicate molecule-ions. Thus, the structure principles described here should be applicable with only minor modifications to silicate and other glasses.

Other Applications.—In this paper it is shown that, in a reorganizing system where there is not only exchange of parts between the molecular units but where the parts themselves can change roles (such as an end group turning into a middle group), the charge on the molecule determines not only the flexibility of the molecular structure but the relative proportions of the building units of which it is assembled. Obviously, these ideas are applicable to a large number of systems other than the phosphates. In phosphorus chemistry, these ideas should be directly applicable to the phosphonitrilic chlorides[16] and their derivatives as well as to the condensed phosphoryl halides.[17] Presumably, they also can be used in discussing structures of the lower oxyacids (also their salts and esters) in which a number of phosphorus atoms are involved in the structure.[18] An even further extension in this field is to the amorphous phosphorus hydrides[19] having over-all empirical compositions ranging from PH to nearly pure P.

Although ester interchange is very slow in the orthophosphates, it is to be presumed that at least P–O–P linkages will make and break rather rapidly in the esters of the condensed phosphoric acids, especially at elevated temperatures, say, around 150°. Investigation of the structure of these esters—presumably by chromatography in non-aqueous solvents—should be carried out so that the results can be compared with the theory given here. A more interesting case than the mixed sodium–hydrogen phosphate glasses discussed above would be phosphates having various proportions of methyl groups and tetramethylammonium ions over a range of values of R. Study of this proposed system would put the relationship between the structural-unit equilibrium constants and the ionic character of the M–O bond on a more firm quantitative basis.

Although structural reorganization of the general type discussed in this paper has been primarily studied in the case of organic compounds,[6] we believe that this type of system will be found to be extremely common in inorganic chemistry, where chemical bonds are at least as labile as the C–O–C linkages in polyesters. Presumably, many common inorganic systems, such as hydrated ferric oxide, are at reorganization equilibrium. The problem is now to prove this broad hypothesis.

DAYTON, OHIO

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[14] Talk by J. R. Van Wazer at the Gordon Research Conference on Glass at Kimball Union Academy, Meriden, N. H., Aug. 14, 1955. Although this 1955 talk was essentially a duplicate of an American Physical Society lecture in 1950 [see *Bull. Am. Phys. Soc.*, **25**, No. 5, 24 (1950)], the idea that glasses exhibited structures similar to those of organic polymers (especially polyelectrolytes) came as a distinct shock to many glass technologists at the Gordon Research Conference.

[15] W. H. Zachariasen, THIS JOURNAL, **54**, 3841 (1932); *J. Chem. Phys.*, **3**, 162 (1935).

[16] L. F. Audrieth, R. Steinman and A. D. R. Toy, *Chem. Revs.*, **32**, 99 (1943).

[17] Unpublished work by J. H. Payne and L. C. D. Groenweghe; R. Klement and K. H. Wolf, *Z. anorg. allgem. Chem.*, **282**, 149 (1955). Also see H. Roux, E. Thilo, H. Grunze and M. Viscontini, *Helv. Chim. Acta*, **38**, 15 (1955).

[18] B. Blaser, Abst. Papers, 129th Meeting Am. Chem. Soc., Dallas, Texas, April 8–13, 1956, pp. 1Q and 8Q.

[19] E. C. Evers and E. H. Street, THIS JOURNAL, **78**, 5726 (1956).