be expected on the basis of the most uniform distribution of the counterions. Thus, a tripolyphosphate composed of two fluorine-free end groups and a fluorophosphate middle group would exhibit a very unequal charge distribution— negative charges on both ends with none in the middle of the molecule–ion. Reorganization should not allow this state of affairs to persist.

To summarize, it seems logical to assume that the new structure building unit is a monofluorophosphate end group (see formula 12-A), although there is no definite proof for this idea. If this assumption is in error, the over-all picture of the $H_2O$–$HF$–$P_2O_5$ system presented herein is essentially unaltered. By this argument, neither difluorophosphate end groups, fluorophosphate middle groups or branching points are to be expected in appreciable amounts in the $H_2O$–$HF$–$P_2O_5$ system.

**Commercial Fluorophosphates.**—In order to inform other investigators about the purity of commercial fluorophosphates, we are reporting some values obtained on commercial samples during the course of this work. The analyses reported here were carried out by the nuclear magnetic resonance technique on stock samples obtained from the Ozark–Mahoning Company of Tulsa, Oklahoma. The data are presented in Table IV. It is interesting to note that qualitative paper chromatographic studies agree with the results presented in this table.

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# Principles of Phosphorus Chemistry. V. Reorganization of Quadruply Connected Monophosphorus Compounds. Part A. The Phosphoryl and Thiophosphoryl Halides

BY LEO C. D. GROENWEGHE AND JOHN H. PAYNE, JR.

Reorganization to form the mixed halides in the two systems $POCl_3$–$POBr_3$ and $PSCl_3$–$PSBr_3$ was quantitatively investigated by means of nuclear magnetic resonance (n.m.r.). The behavior of both systems approached that calculated for a completely random reorganization with equilibrium being achieved in less than one week at 130°. The mixed halides, $POClBr_2$, $POCl_2Br$, $PSClBr_2$ and $PSCl_2Br$ can be made in yields of over 40% by heating mixtures of $POCl_3$ and $POBr_3$ or of $PSCl_3$ and $PSBr_3$ for a few hours at temperatures of above 200°. It is shown that, under suitable conditions, the percentage of the total phosphorus present as a given compound in a mixture can be determined by n.m.r. to within better than ±1 mole %.

Structural reorganization based on exchange of ligands attached to the phosphorus atom is a common phenomenon in the chemistry of phosphorus compounds. In many respects, compounds based on $sp^3$ hybrids of phosphorus are similar to organic compounds based on $sp^2$ hybrids of carbon. This similarity may, at least in part, be attributed to π-bonding, a subject which was discussed in the first paper[1] of this series. The similarity is exemplified by the reorganization process, since many compounds based on a single phosphorus atom undergo reorganization about as rapidly as do organic esters and the reorganization of organic polyesters finds many parallels in phosphorus chemistry.[2]

In a number of forthcoming papers in this series, we shall attempt to outline the principles involved in reorganization of phosphorus compounds and to describe a sufficient number of examples to prove how general this behavior is. The present paper is concerned with reorganization equilibrium in two related systems based on a single phosphorus atom per molecule: $POCl_3$–$POBr_3$ and $PSCl_3$–$PSBr_3$.

## Experimental Section

The phosphorus oxychloride $POCl_3$ used in these experiments was redistilled from the Monsanto commercial-grade product. The phosphorus oxybromide $POBr_3$ was purchased. Nuclear magnetic resonance measurements showed that this sample contained about 5% of the phosphorus as phosphorus tribromide. Since this was a relatively small amount of impurity which could be accounted for in our studies, the sample was used without further purification.[3]

The thiophosphoryl chloride was made from phosphorus trichloride and sulfur according to the method of Inorganic Syntheses.[4] The thiophosphoryl bromide also was prepared according to the method of Booth and Seabright.[5] The product had a sharp melting point at 38°.

Reorganization was carried out by weighing the desired proportions of the trichloride and tribromide and sealing them in a thick-walled Pyrex tube which was held in an oven at 130° after thorough mixing. It was found that in an hour's time, the phosphoryl halide system reorganized so as to give about 5% of the amount of mixed oxyhalides expected at equilibrium, whereas, in the thiophosphoryl halide system, only a trace of the mixed halides was found.

(1) J. R. Van Wazer, THIS JOURNAL, **78**, 5709 (1956).

(2) J. R. Parks and J. R. Van Wazer, *ibid.*, **79**, 4890 (1957).

(3) This small amount of $PBr_3$ has been weighed as $POBr_3$ and has only a slightly smaller molecular weight. It reorganizes with the chlorine-containing molecules to give an equilibrium similar to the quadruply connected molecules, making practically the desired ratio of Cl:Br atoms available for the study.

(4) T. Moeller, H. J. Birch and N. C. Nielsen, "Inorganic Syntheses," Vol. IV, McGraw-Hill Book Co., New York, N. Y., 1953, p. 71.

(5) H. S. Booth and C. A. Seabright, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., New York, N. Y., 1946, p. 153.

The samples were kept in the oven for one week, quickly cooled and measured, returned to the oven for another week at the same temperature and then cooled quickly and measured for a second time. Since the measurements showed no appreciable change in composition before and after the second week of heating, the results reported here should represent equilibrium values. The samples were cooled rapidly (from 130° to room temperature within 5 minutes) so that the results would represent equilibria at the oven temperature of 130°.

The samples were analyzed by n.m.r. measurements. The P[31] spectra were obtained by utilizing the intermediate-passage absorption-mode presentation. A Varian high-resolution spectrometer, Model No. V-4300B, was used with a 16.2 mc. radiofrequency and a magnetic field of about 9395 gauss (Varian magnet Model No. V-4012-HR). In both the POCl$_3$–POBr$_3$ and the PSCl$_3$–PSBr$_3$ systems only four resonance peaks were found as expected: the two end members (pure halides) and the two mixed halides.

The chemical shifts of the resonance peaks were determined by the tube interchange technique and are reported in parts per million (p.p.m.) using 85% H$_3$PO$_4$ as a standard. Quantitative analysis was made by measuring the areas under the peaks. Apeco-Autostat copies were made from two different n.m.r. spectra of the same sample, and the peaks were cut from these copies and weighed. Since the resonances of the peaks were as far apart as 140 p.p.m., it was necessary to correct the results obtained for deviations in the sweep linearity of the magnetic field as determined by putting about 200 c.p.s. sidebands on the spectrum (audio-signal). This resulted in a correction of up to 13% of the area. The corrected areas were taken to be proportional to the fraction of the total phosphorus in the various compounds.

## Results and Discussion

The phosphoryl chloride–bromides[6] and the thiophosphoryl chloride–bromides[7] have been previously prepared in the pure form. More recently, all possible mixed oxy- and thiophosphoryl halides of fluorine, chlorine and bromine of the type POX$_3$ and PSX$_3$ have been prepared as mixtures which were identified by Raman spectra.[8]

Since the n.m.r. peaks corresponding to the mixed chloride–bromides were found to maximize at the appropriate mixture of end members, assignments of the n.m.r. of the mixed halides were easily made (Table I). Further proof of these assignments rests on the fact that the stoichiometry of the systems could not be made to agree with any other assignment.

Table I

Nuclear Magnetic Resonance Frequencies of Oxy- and Thiophosphoryl Chloride–Bromides[9]

| Compound | Freq. p.p.m. | Compound | Freq. p.p.m. |
|---|---|---|---|
| POCl$_3$ | − 2.2 | PSCl$_3$ | − 28.8 |
| POCl$_2$Br | + 29.6 | PSCl$_2$Br | + 14.5 |
| POClBr$_2$ | + 64.8 | PSClBr$_2$ | + 61.4 |
| POBr$_3$ | +103.4 | PSBr$_3$ | +111.8 |

The random-reorganization theory developed for mixtures of polyphosphates[2] can be applied to monophosphorus compounds, such as the halide mixtures in equilibrium. According to this theory, all exchange reactions in the oxyhalide and thiohalide systems are represented by the
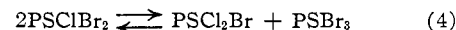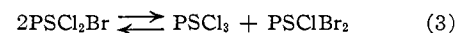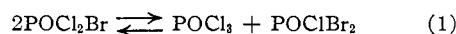
(6) N. Menschutkin, *Liebig's Ann.*, **139**, 345 (1866); *Bull. soc. chim.*, **6**, 481 (1866); A. Besson, *Compt. rend.*, **122**, 814 (1896).

(7) A. Besson, *Compt. rend.*, **122**, 1058 (1896); A. Michaelis, *Ber.*, **5**, 6 (1872).

(8) M. L. Delwaulle and Felix François, *J. chim. phys.*, **46**, 87 (1949).

(9) N. Muller, P. C. Lauterbur and J. Goldenson, This Journal, **78**, 3557 (1956), reported the chemical shifts of POCl$_3$, POBr$_3$, PSCl$_3$ and PSBr$_3$ to be, respectively, −1.9, +102.9, −28.8 and +111.8.

equations

$$2POCl_2Br \rightleftharpoons POCl_3 + POClBr_2 \quad (1)$$

$$2POClBr_2 \rightleftharpoons POCl_2Br + POBr_3 \quad (2)$$

$$2PSCl_2Br \rightleftharpoons PSCl_3 + PSClBr_2 \quad (3)$$

$$2PSClBr_2 \rightleftharpoons PSCl_2Br + PSBr_3 \quad (4)$$

Under the conditions employed, the various compounds come in equilibrium with each other, and the equilibrium constants can be calculated

$$K_{1,o} = [POCl_3][POClBr_2]/[POCl_2Br]^2 \quad (5)$$

$$K_{2,o} = [POCl_2Br][POBr_3]/[POClBr_2]^2 \quad (6)$$

$$K_{1,s} = [PSCl_3][PSClBr_2]/[PSCl_2Br]^2 \quad (7)$$

and

$$K_{2,s} = [PSCl_2Br][PSBr_3]/[PSClBr_2]^2 \quad (8)$$

The quantitative data obtained from five different chloride to bromide ratios in both the oxygen and the sulfur-containing compounds are shown, respectively, in Figs. 1 and 2. These figures show that if one heats mixtures of POCl$_3$ and POBr$_3$ or of PSCl$_3$ and PSBr$_3$ in either a 2:1 or a 1:2 mole ratio, one obtains mixtures which contain 42% of POCl$_2$Br, 46% of PSCl$_2$Br or 44% of POClBr$_2$, 42% of PSClBr$_2$ depending on the mixture treated. These results show that it is very easy to make the mixed phosphoryl and thiophosphoryl halides in substantial yields. A heating period of a few hours at a temperature above 200° should be sufficient to reach the desired equilibrium. Previous authors[6,7] have reported that such phosphoryl halide mixtures can be separated readily by fractional distillation under reduced pressure.

The results of all the samples obtained from the duplicate n.m.r. spectra were statistically analyzed. When the results were expressed in percentage

Table II

Equilibrium Constants for Various Cl/P Atom Ratios

| Cl/P ratio from | | | Calcd. equil. const. | | |
|---|---|---|---|---|---|
| N.m.r. | Ratio of reagents | $K_1$ | $\Delta K_1{}^a$ | $K_2$ | $\Delta K_2{}^a$ |
| POCl$_3$–POBr$_3$ mixt. in equil. | | | | | |
| 0.35 | 0.36 | ... | ... | 0.415 | 0.057 |
| 0.79 | 0.76 | 0.593 | 0.126 | .315 | .016 |
| 1.49 | 1.49 | .387 | .020 | .372 | .020 |
| (1.45)$^c$ | (1.49) | (.291) | (.018) | (.367) | (.019) |
| 2.23 | 2.25 | .413 | .017 | .406 | .111 |
| 2.69 | 2.67 | .445 | .071 | ... | ... |
| Weighted-av. $K$'s$^b$ | | .406 | .013 | .341 | .012 |
| PSCl$_3$–PSBr$_3$ mixt. in equil. | | | | | |
| 0.35 | 0.39 | ... | ... | 0.427 | 0.095 |
| 1.01 | 1.00 | 0.319 | 0.079 | .420 | .028 |
| 1.55 | 1.50 | .306 | .026 | .399 | .038 |
| 1.54 | 1.50 | .299 | .025 | .446 | .041 |
| (1.52)$^c$ | (1.50) | (.248) | (.023) | (.430) | (.039) |
| 1.99 | 2.00 | .253 | .017 | .356 | .100 |
| 2.64 | 2.62 | .414 | .085 | ... | ... |
| Weighted-av. $K$'s$^b$ | | .297 | .012 | .419 | .019 |

$^a$ $\Delta K$ is the standard error computed statistically from differences of Cl/P ratio calculated from the ratio of reagents (taken as the true value) and from n.m.r. data. $^b$ Weighted average $K$'s are obtained from the formula: $K = \Sigma K_i W_i / \Sigma W_i$, where $W_i = 1/\Delta K_i{}^2$. The weighted $\Delta K$ is derived from $\Delta K = 1/\sqrt{\Sigma W_i}$. $^c$ Values between parentheses are derived from equilibria obtained after one week at 130° and are not included in the computation for the weighted average of $K$.
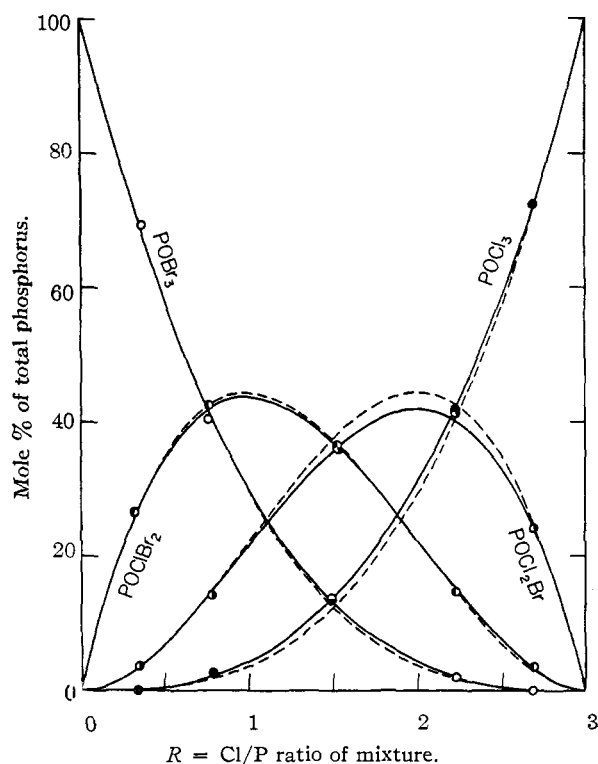
Fig. 1.—Equilibria of $POCl_3$–$POBr_3$ randomly reorganized mixtures. The solid lines correspond to $K_{1,o} = 0.406$ and $K_{2,o} = 0.341$; the dotted lines correspond to the completely random case in which $K_1 = K_2 = 0.333$.



Fig. 2.—Equilibria of $PSCl_3$–$PSBr_3$ randomly reorganized mixtures. The solid lines correspond to $K_{1,s} = 0.297$, $K_{2,s} = 0.419$; the dotted lines correspond to the completely random case in which $K_1 = K_2 = 0.333$.

of the total phosphorus present, the absolute standard deviation for the average of two measurements on a single peak in the oxygen- and sulfur-containing systems were, respectively, 0.33 and 0.51 mole %. The greater accuracy of the measurement in the oxygen-based system can be explained by the fact that the chemical shift between the end members in the n.m.r. spectrum is smaller (see Table I), and, therefore, the errors in the corrections for sweep non-linearity were less important.

A statistical comparison was made between the Cl/P atom ratio as calculated from the n.m.r. data, and the same ratio as calculated from the weight of the starting materials (Table II) assuming negligible weighing errors. Translating these data back into terms of an average of two measurements of a single peak revealed an absolute standard deviation of 0.55 and 0.90 mole % for the oxygen- and the sulfur-containing compounds, respectively. These results indicate that a definite bias is introduced for both systems, presumably in determining the sweep linearity of the magnetic field. The latter standard deviations have been used in weighting the data to calculate the best value for the equilibrium constants and to assign their standard deviations given in Table II.

Table II also shows that for compositions obtained after two weeks of heating at 130°, the individual $K$ values as compared to the corresponding weighted-average $K$'s fall within the standard deviations two-thirds of the time. This indicates that these constants are truly invariant
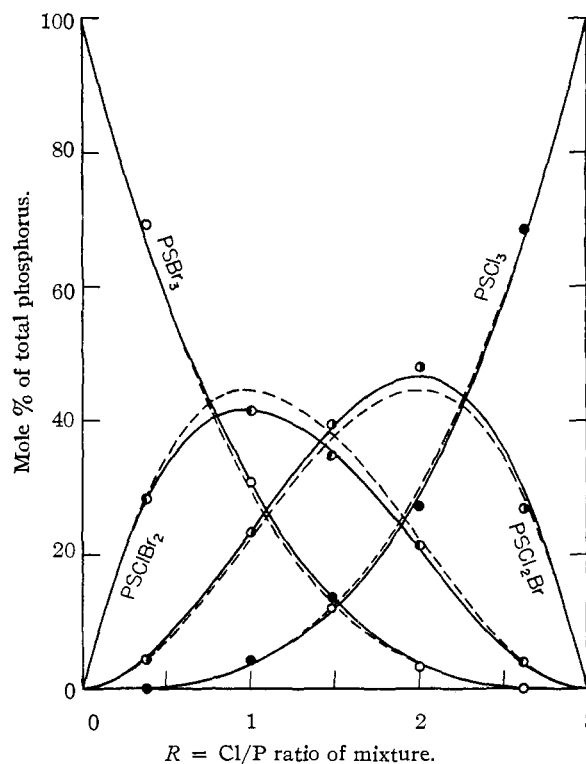
and independent of changes in the Cl/P ratio. The fact that the $K_{1,o}$ obtained after one week of heating has a significant error cannot be attributed to failure to reach equilibrium because less than the equilibrium amount of the $POCl_3$ starting material was found.

The constancy of the $K$ values shows that the activity coefficients for the various reorganizing compounds are equal and do not change with composition so that they can be set equal to unity. Such ideal solutions are to be expected for these closely related compounds. If it is assumed that the bond energy (enthalpy) of the P–Cl and P–Br bonds are independent of the other atoms to which the phosphorus atom is attached, then the heat of reorganization should be zero and the equilibrium constant must be independent of temperature. The free energy and entropy of reorganization would not be zero but would be governed exclusively by probability.

In the case of completely random distributions for which the Cl/Br atom ratio is $p/q$, (with $p + q = 1$), the probability of having a phosphorus atom with $n$ chlorine atoms and $3 - n$ bromines in the three positions subject to random reorganization is

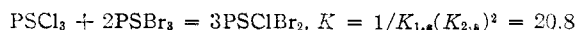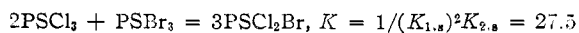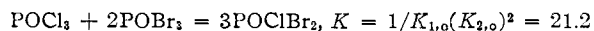$$P_3(n) = \frac{3!}{n!(3 - n)!}\, p^n \cdot q^{(3-n)} \qquad (9)$$
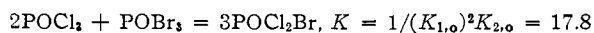
for $n = 0$, 1, 2, or 3. Values thus obtained can be substituted in equations 5–8 for $K_1$ and $K_2$. The $p$ and $q$ terms drop out giving

$$K_1 = K_2 = 1/3 \qquad (10)$$

It should be pointed out that the earlier presenta-

tion[2] of the non-ionic system, while qualitatively correct, incorrectly assumed that $K_1 = K_2$ was equal to unity.

From Table II, it is apparent that the equilibria are not quite random. Perhaps the best way of comparing the stability of the various mixed halides is to compare their formation constants from the pure halides

$2POCl_3 + POBr_3 = 3POCl_2Br, K = 1/(K_{1,0})^2K_{2,0} = 17.8$

$POCl_3 + 2POBr_3 = 3POClBr_2, K = 1/K_{1,0}(K_{2,0})^2 = 21.2$

$2PSCl_3 + PSBr_3 = 3PSCl_2Br, K = 1/(K_{1,s})^2K_{2,s} = 27.5$

$PSCl_3 + 2PSBr_3 = 3PSClBr_2, K = 1/K_{1,s}(K_{2,s})^2 = 20.8$

Since a mixed halide found in a completely randomly-reorganized equilibrium would have a formation constant of 27 (corresponding to $K_1 = K_2 = 1/3$), it is evident that the end members of these systems are slightly preferred except for the case of $PSCl_2Br$.

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# Principles of Phosphorus Chemistry. VI. Reorganization of Quadruply Connected Monophosphorus Compounds. Part B. The Chlorophosphoric Acids

BY JOHN R. VAN WAZER AND EKKEHARD FLUCK[1]

Mixtures of phosphoric acid and phosphorus oxychloride react in sealed tubes at 25 and 110° to give a variety of products. When the mole % of phosphorus oxychloride is greater than 50, the main reaction product is dichlorophosphoric acid; when it is smaller than *ca.* 60, free hydrogen chloride and condensed species form. The resulting condensed species are made up of regular phosphate end groups, monochlorophosphate end groups, dichlorophosphate end groups and regular phosphate middle groups. For mole % of phosphorus oxychloride ranging from 15 to 60, some of the free hydrogen chloride forms a separate phase. Very small amounts of monochlorophosphoric acid were detected at equimolar amounts of the reagents. At temperatures of 230° and above, all of the chlorine for a mole % of phosphorus oxychloride below 50 is found as free hydrogen chloride in a separate phase. The data at 25 and 110° were found to agree with reorganization theory, which predicts essentially pure dichlorophosphoric acid when one mole of phosphoric acid plus two moles of phosphorus oxychloride reach equilibrium. Various alternative preparations of dichlorophosphoric were also shown to give an essentially pure product at equilibrium, as determined by the nuclear magnetic resonance (n.m.r.) technique used in this study. The system formed by mixing phosphoric acid with triphenyl phosphate was qualitatively found to reorganize approximately as predicted theoretically.

In Part A of this paper, two examples were given of the reorganization between un-ionized compounds based on a single phosphorus atom. In this paper, a more complicated situation is presented. In the system made by combining various proportions of orthophosphoric acid with orthophosphoryl chloride, condensation competes with reorganization. Furthermore, the reorganization represents the case where an un-ionized structure, orthophosphoryl chloride, is in equilibrium with various ionized structures: orthophosphoric acid and its chloro derivatives as well as the condensed phosphoric acids and their chloro derivatives. Another example of reorganization between ionized and un-ionized molecules is found in the system made by combining various proportions of orthophosphoric acid with triphenyl orthophosphate. Some qualitative data on this system are reported herein.

## Experimental Section

The general procedures described in Part A of this paper[2] were employed here. However, no sweep non-linearity corrections were made in the n.m.r. measurements. The orthophosphoryl chloride, $Cl_3PO$, and triphenyl phosphate, $(C_6H_5O)_3PO$, were Monsanto products and each showed only the single n.m.r. peak corresponding to that compound. The 100% orthophosphoric acid, $(HO)_3PO$, was obtained by

evaporating 85% Monsanto commercial-grade phosphoric acid in high vacuum at 75° for six days. After this time, the majority of the sample crystallized upon cooling to room temperature. The crystalline fraction was separated and employed in these experiments.

**The $H_3PO_4$-$POCl_3$ System.**—Mole ratios of Cl/P (the $R$ value[3]) corresponding to 0.375, 1.00, 1.50, 2.00 and 2.63 were prepared by weighing out the proper amount of crystalline phosphoric acid and adding to this the correct volume of orthophosphoryl chloride. All samples were contained in sealed, thick-walled glass tubes which were stored at the four different temperature of 25, 110, 230 and 300°. The contents of the tubes were continuously agitated during the storage period. At 25°, this was effected by an oscillating shaker table. At 110 and 230°, the glass tubes were put into sections of iron pipe which were rotated end over end in an oven. The glass tubes studied at 300°, and some tubes studied at 230°, were put into a rocking autoclave with different outside pressures to prevent explosion of the tubes. Although a number of different conditions were tried, the majority of the tubes exploded. The undamaged tubes at 230° corresponded to $R = $ Cl/P $= 0.375, 1.00$ and $2.63$; whereas, at 300°, the only tube rescued was the one corresponding to $R = 1.50$.

At room temperature, it was found that the crystalline phosphoric acid took three to four days to dissolve. In the tube for which $R = $ Cl/P $= 1.0$, a separate phase of hydrochloric acid began to appear after fourteen days had elapsed. After two months, and after five months, n.m.r. measurements were carried out on the tubes held at 25°. The two-month and five-month results were identical so that it was assumed that they represented equilibrium or, at least, metastable conditions. The tubes held at 110° were measured after 120 hr. and after 168 hr., and again both sets of measurements agreed. Since the tubes were cooled as rapidly

(1) On leave from Heidelberg University, Germany, during the academic year of 1957–1958.

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

(3) J. R. Van Wazer, *ibid.*, **72**, 644 (1950); J. R. Parks and J. R. Van Wazer, *ibid.*, **79**, 4890 (1957).