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

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

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

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

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

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 $PSCl_2Br$.

Acknowledgments.—The authors wish to express their appreciation to John R. Parks and Allan Dickinson for their help on the mathematical treatment of this paper. Gratitude is also due to Dr. Donald P. Ames for his assistance and instruction in n.m.r. techniques

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

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]

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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

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(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).

as possible (several minutes to go from 110 to 25°), and the n.m.r. measurements were carried out promptly thereafter (within the same day) on the sealed tubes, it is believed that these measurements correspond to the conditions prevailing at 110°. The tubes held at 230 and 300° were measured after 65 hr. at the respective temperatures and were also cooled to room temperature within a few minutes and measured promptly without unsealing the tubes.

In some of the sealed tubes, two phases were seen. The top layer was always very fluid as compared to the lower layer and was found to evaporate rapidly and completely, immediately upon opening the tube at −70°. Some of this gas was condensed at an even lower temperature and was found to exhibit a boiling point of −85°. This is adequate proof that the upper layer in these tubes consisted of reasonably pure, liquid hydrogen chloride. At 25 and 110°, this phase separation was only noted for the tubes exhibiting $R = Cl/P = 1.00$ and 1.50. At 25°, there were 15.9 wt. % and 5.0 wt. % in the separate HCl phase for $R = 1.00$ and 1.50, respectively. None of the other composition ratios studied exhibited a detectable amount of a separate phase of hydrogen chloride.

The compositions corresponding to $R = Cl/P = 0.375$ and 1.00 at 230° exhibited two phases. In this case, all of the chlorine was found to be in the hydrogen chloride layer with only condensed phosphoric acids free of chlorine in the other, more viscous phase. The one tube ($R = 1.50$) at 300° acted the same way, giving liquid HCl and a granular white powder having an appearance similar to that of ammonium chloride. After evaporation of the hydrogen chloride at room temperature, the white powder was found to be free of chlorine by the silver nitrate–nitric acid test. Unfortunately, the powder was lost in an accident before an X-ray powder diagram was taken. It must have been phosphorus pentoxide, formed according to the classical equation

$$H_3PO_4 + POCl_3 \xrightarrow{\Delta} 3HCl + P_2O_5 \qquad (1)$$

In the n.m.r. measurements, seven different resonance peaks were observed and assigned chemical shifts.[4] Since one of these peaks, at *ca.* −1.5 p.p.m. from the peak of 85% H_3PO_4, was found to maximize at R values of 0 and 3 and to go to zero at $R = 1.5$, it was attributed to both phosphoric acid and orthophosphoryl chloride which were not expected to occur concomitantly. The peak which appeared at −9.5 p.p.m. for $R = 2.00$ and at −10.5 p.p.m. for other values of R was easily assigned to dichlorophosphoric acid, $(HO)Cl_2PO$, since it represented 93% of the phosphorus at the $R = 2$ composition corresponding to $(HO)Cl_2PO = H_3PO_4 \cdot 2POCl_3$ and approached zero at $R = 0$ and 3. The assignment of the peak corresponding to the phosphate end group, $(HO)_2OPO_{1/2}-$, was also relatively straightforward since this is a well-known peak and it was found to maximize toward the phosphoric acid end of the diagram. It is interesting to note that the end-group peak in this system is about 2 p.p.m. more positive than is the end-group peak in dilute aqueous solutions. The peak corresponding to the middle group, $-O_{1/2}(HO)P(O)O_{1/2}-$, was assigned only after considerable deliberation, since it appears *ca.* 9 p.p.m. higher than the peak corresponding to this middle group in aqueous solution.[4] As shown in Paper VII of this series, the observed resonance is very close to that found for chlorophosphate middle groups, $-O_{1/2}(Cl)P(O)O_{1/2}-$. The fact that the observed resonance maximizes at the over-all chemical composition at which the formation of a separate HCl phase was a maximum indicates that it corresponds to middle groups. The relatively large amount of HCl in the separate phase rules out chlorophosphate middle groups. The three most difficult peaks to identify appeared at −18.2, −13.0, and +8.3 p.p.m. These were finally tentatively assigned to monochlorophosphoric acid, $(HO)_2ClPO$; the monochlorophosphate end group, $(HO)ClP(O)O_{1/2}-$; and the dichlorophosphate end group, $Cl_2(O)PO_{1/2}-$, respectively. In Paper VII of this series, the dichlorophosphate end group is unequivocally identified at +8.5 ± 0.5 p.p.m.

The main basis for belief in the assignments made for the n.m.r. peaks observed in this study lies in the fact that these assignments agreed with the stoichiometry of the system. Material balances were carried out on phosphorus, chlorine and hydrogen, and were found to agree, within experimental error, with the amounts of these elements present when the n.m.r. peak assignments described above were employed. Thus, the main proof for the presence of the monochlorophosphoric acid end group, the dichlorophosphate end group, and monochlorophosphoric acid as well as the regular middle group in the system studied here is the material balance at $R = Cl/P = 1.5$. All other assignments of reasonable structures based on sp^3 hybridization of the phosphorus were tried and found not to fit.

Other Systems.—The systems obtained by combining various proportions of orthophosphoric acid with triphenyl orthophosphate or orthophosphoryl chloride with triphenyl orthophosphate were investigated in a preliminary manner, following general procedures described above. However, in both of these systems, there were considerable side reactions involving the phenyl groups. After heating for 18 days at 300°, the $POCl_3$–$(C_6H_5O)_3PO$ system gave n.m.r. traces corresponding to partial equilibration between the oxyhalide, the two chlorophosphate esters and the neutral ester: However, after extensive heating (three months at 300°), the tube for which $R = Cl/P = 1.5$ was seen to be filled with a doughy, brown mass. Unidentified organic compounds not containing phosphorus were found. The complicated, predominantly uninterpreted n.m.r. spectra of the mixture of phosphorus-containing species gave evidence for the probable occurrence of oxidation–reduction reactions.

Although there was no evidence for or against oxidation–reduction reactions in the H_3PO_4–$(C_6H_5O)_3PO$ system, the rates of the side reactions appeared to be nearly as rapid as the rates of reorganization of phenoxy and "hydroxyl" groups. Thus, after heating for one month at 200°, the tube exhibiting $R = C_6H_5O/P = 0.375$ showed about 25% by volume of a separate organic phase not containing phosphorus. For values of $R = C_6H_5O/P$ in the range of 1.6 to 2.6 about 8–10% of the total phosphorus was present in two unidentified compounds.

The Orthophosphoric Acid-Orthophosphoryl Chloride System

The results of this study are completely depicted in Fig. 1, in which the percentage of the total phosphorus present in the various species is given as a function of the composition of the system. The curve (I) corresponding to free hydrochloric acid as well as the short line to the lower left-hand side of the diagram corresponding to free water (curve X) is derived by difference and was not measured directly. The intercepts on the axis corresponding to pure phosphoric acid were taken from a study[5] (which has been checked in our laboratory) of the compositions of various phosphoric acids.

Curve J in Fig. 1 delineates the composition area corresponding to a phase separation of the hydrogen chloride. Although this area was based on only three points (one of which was zero), it is believed to be reasonably correct, since the solubility of the HCl was found (according to the difference between curves I and J) to increase gradually when going toward the phosphoric acid end of the diagram, as would be expected.

Since it was found that the measurements at 25 and 110° agreed with each other within experimental error, Fig. 1 depicts the equilibrium at both temperatures. This "equilibrium" may only represent metastability since, in samples for which $R < 1.5$ that were quickly cooled from higher temperatures (230° and above), all of the chlorine was found in a separate hydrogen chloride phase.

The explanation of the results described in Fig. 1 is relatively straightforward—with two main factors being at work. The first factor, which

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[4] J. R. Van Wazer, C. F. Callis, J. N. Shoolery and R. C. Jones, THIS JOURNAL, **78**, 5715 (1956); J. R. Van Wazer, C. F. Callis and J. N. Shoolery, *ibid.*, **77**, 4945 (1955).

[5] A. L. Huhti and P. A. Gartaganis, *Can. J. Chem.*, **34**, 785 (1956).

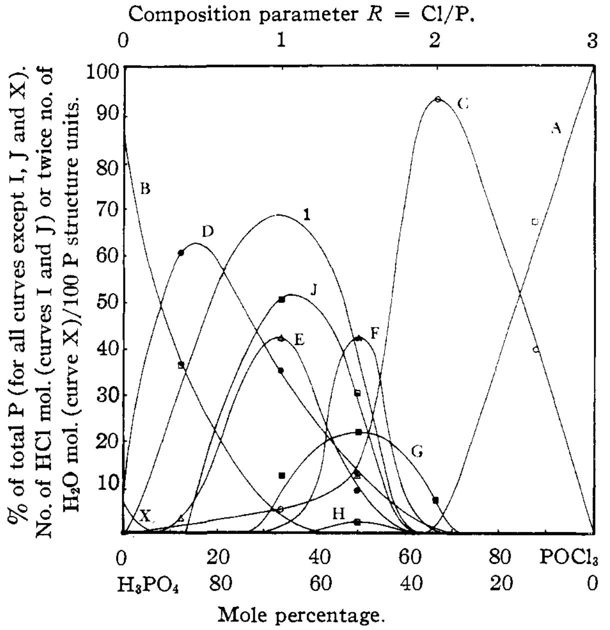

Fig. 1.—Equilibrium (perhaps metastable) in the liquid system H_3PO_4-$POCl_3$ at 25 and 110°, the system being kept under pressure to prevent loss of hydrogen chloride. A = Cl_3PO, B = $(HO)_3PO$, C = $(HO)Cl_2PO$ (dichlorophosphoric acid), D = $(HO)_2OPO_{1/2}$-(phosphate end group), and E = $-O_{1/2}(HO)P(O)O_{1/2}$-(phosphate middle group). F is probably $Cl(HO)P(O)O_{1/2}$-(monochlorophosphate end group), G is probably $Cl_2(O)PO_{1/2}$-(dichlorophosphate end group) and H is probably $(HO)_2ClPO$ (monochlorophosphoric acid). I represents total free hydrogen chloride obtained from the material balance, J is the free hydrogen chloride present as a separate phase and X is free water.

plays the major role at the left side of Fig. 1, is phosphate condensation concurrent with formation of free hydrogen chloride. The thermodynamics of phosphate systems is such that H_2O of composition is avidly held but HCl of composition is easily lost. This explains the fact that, when condensed phosphates free of chlorine are boiled with water, hydrolysis occurs to give the orthophosphate, whereas, when orthophosphoryl chloride is added to water, condensed phosphates free of chlorine can be formed.[2] In the first case, degradation occurs because water is taken up by the phosphorus-containing molecules and, in the other, condensation occurs because HCl is released. Work with any of the chlorophosphates, including orthophosphoryl chloride, indicates the undesirability of the often-used phrase "molecularly dehydrated phosphates" to describe the condensed phosphates, since condensed phosphates can be made by molecularly hydrating chlorophosphates.

The other factor, which is of major importance on the right-hand side of Fig. 1, is the matter of detailed balancing of charges—a subject which has been emphasized in previous publications from this Laboratory.[3] All of the phosphate species shown in Fig. 1 are ionized except for the orthophosphoryl chloride and the tentatively assigned dichlorophosphate end group. It seems reasonable that in the highly condensed system under study, all of the ionized species will bear about the same electrical charge (approximately a single negative charge). Thus, for example, the single hydrogen of dichlorophosphoric acid is more strongly dissociated than any of the hydrogens of phosphoric acid, but there are three of the latter so that the effective ionization in this condensed system may be about the same. An equation for the reorganization of the dichlorophosphate anion into the orthophosphate species having one more chlorine and the species having one less chlorine is

$$H^+ + 2PO_2Cl_2^- \longleftarrow POCl_3^0 + PO_2Cl(OH)^- \quad (2)$$

The equilibrium for this equation should be very far to the left since it represents the conversion of two structures bearing single negative charges, into one with no charge, and another with a single charge—a situation which, obviously, leads to a detailed unbalance of charge in the reorganizing amorphous system.

The fact that 7% of the phosphorus at the dichlorophosphoric acid composition is present in condensed phosphates indicates that the driving force tending toward detailed balancing of charge is considerably stronger than the driving force due to dehydrohalogenation. The presence of the dichlorophosphate end group and the possible presence of the chlorophosphate middle group is attributable to the stoichiometry of the system. The smallness of the amount of monochlorophosphoric acid found in this system is due to the fact that its reorganization to neighboring species in the system involves no change of charge, so that dehydrohalogenation becomes the controlling factor.

A brief study was made of the kinetics of formation of dichlorophosphoric acid from the appropriate mixture of orthophosphoryl chloride and phosphoric acid. In this work, the crystalline orthophosphoric acid was heated to its melting point and the resulting liquid was mixed quickly with the orthophosphoryl chloride. The steps of heating, mixing and subsequent cooling to room temperature were carried out in about a minute, and the resulting system was a single-phase liquid throughout the entire experiment. Although some dichlorophosphoric acid formed promptly (within an hour), there was considerable build-up of condensed species with concomitant formation of free hydrochloric acid (which did not result in a phase separation). From the data, it was estimated that a maximum in the formation of hydrogen chloride occurred after about 75-100 hr. at 25°. The starting materials were found to practically disappear in the first few hours and the reaction between the hydrogen chloride and the condensed species to give the final equilibrium amount of dichlorophosphoric acid was still proceeding at an appreciable rate after a month at 25°.

Dichlorophosphoric Acid

Although they had practically no evidence for its existence, Meerwein and Bodendorf described[6] a preparation of dichlorophosphoric acid in 1929. No further work was reported on this compound until last year when three papers appeared.[7,8]

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(6) H. Meerwein and K. Bodendorf, *Ber.*, **62**, 1952 (1929).

(7) J. Goubeau and P. Schulz, *Z. anorg. allgem. Chem.*, **294**, 224 (1958); *Z. physik. Chem.*, **14**, 49 (1958).

(8) H. Grunze and E. Thilo, *Angew. Chem.*, **70**, 73 (1958).

A quantitative measure of the yield of dichlorophosphoric acid was not made in any of these studies since appropriate physical methods were not available and the problem of separating dichlorophosphoric acid from the by-products of the reaction has not yet been solved. We have repeated these preparations and investigated several other preparations of dichlorophosphoric acid, using nuclear magnetic resonance to evaluate quantitatively the composition of the reaction products. Following Meerwein and Bodendorf,[6] equimolar amounts of orthophosphoryl chloride dissolved in ether were combined with water at room temperature. Following Goubeau and Schulz,[7] equimolar amounts of orthophosphoryl chloride and water were combined, taking care to keep the temperature in the range of −20 to −10°. In addition, we made dichlorophosphoric acid according to the two equations

$$P_4O_{10} + 6H_2O + 8Cl_3PO \longrightarrow 12(HO)Cl_2PO \quad (3)$$

$$P_4O_{10} + 6PCl_5 + 5(HO)_3PO \longrightarrow 15(HO)Cl_2PO \quad (4)$$

The reactions described in equations 3 and 4 were carried out by heating to 230° in a sealed tube for 72 hr.

In all cases, it was found that 93 ± 3% of the total phosphorus occurred as the dichlorophosphoric acid, with the remaining 7 ± 3% being present as a mixture of condensed phosphates (primarily pyrophosphoryl chloride). In other words, the equilibrium shown in Fig. 1 apparently can be achieved by any of these preparation methods. This means that Grunze and Thilo[3] were incorrect in saying that Goubeau and Schulz did not make dichlorophosphoric acid by their procedure. We did not test the procedure of Grunze and Thilo involving the hydrolysis of pyrophosphoryl chloride but see no reason why this also should not give almost pure dichlorophosphoric acid.

We found the density of the 93% dichlorophosphoric acid to be 1.77 g./cc. at 25°. (The other reported density[3] is 1.6878.) Its vapor pressure is 17 mm. at the same temperature as compared to 40 mm. for $POCl_3$. There is a gradual increase in measured pressure, with time, due to evolution of HCl and concomitant formation of condensed phosphoric acids. When dichlorophosphoric acid is heated at atmospheric pressure, it loses HCl with increasing rapidity as the temperature is raised. When heated sufficiently long or sufficiently hot, all of the chlorine can be removed as HCl. Unlike orthophosphoryl chloride, dichlorophosphoric acid is miscible with water. In cold water, it hydrolyzes gently. It is soluble in alcohol and undergoes a reaction therein which probably results in the dialkyl ester of orthophosphoric acid. The odor of dichlorophosphoric acid is similar to that of orthophosphoryl chloride but is less penetrating.

The Orthophosphoric Acid–Triphenyl Orthophosphate System

In spite of the presence of side reactions, the H_3PO_4–$(C_6H_5O)_3PO$ system gave the kind of results to be expected for an uncharged molecule reorganizing with molecule–ions, all bearing approximately a single negative charge. Thus, after one month at 200°, the diphenyl phosphate was found to maximize at a value of $R = C_6H_5O/P = 2$ to give a value of *ca.* 70% of the total phosphorus minus the phosphorus in by-products, as compared to *ca.* 40% of the total phosphorus as monophenyl phosphate at $R = 1$ where the amount of the monophenyl ester reaches a maximum.

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

Principles of Phosphorus Chemistry. VIII. Reorganization of Triply Connected Monophosphorus Compounds

BY EKKEHARD FLUCK,[1] JOHN R. VAN WAZER AND LEO C. D. GROENWEGHE

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Various mixtures of phosphorus trichloride, phosphorus tribromide and triphenyl phosphite were prepared to study the equilibrium between the ten compounds expected from reorganization in this system. All ten compounds, based on triply connected phosphorus, were found, and equilibrium constants for their formation are presented. These equilibrium constants are compared with values calculated on the basis of completely random reorganization, and the system is shown to deviate from the completely random case. This deviation becomes less pronounced as the bromine increases from one to two bromines per phosphorus atom.

As part of a general study of the reorganization process in phosphorus-based compounds, some work has been carried out on the exchange of ligands between simple structures based on triply connected phosphorus. The purpose of this work was to discover whether the reorganization was approximately random and if it followed the same general principles[2] that apply to compounds based on quadruply connected phosphorus. In this work, three related systems were investigated: $P(OC_6H_5)_3$–PCl_3, $P(OC_6H_5)_3$–PBr_3 and PBr_3–PCl_3. These systems were chosen because the work on quadruply connected phosphorus compounds[2] indicated that reorganization would occur reasonably fast in them. This was found to be the case.

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[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); J. R. Van Wazer and E. Fluck, *ibid.*, **81**, 6360 (1959); L. C. D. Groenweghe, J. H. Payne and J. R. Van Wazer, unpublished.