

monoclinic-to-tetragonal transformation of ZrO<sub>2</sub>,<sup>7,8</sup> as well as the behavior of ZrO<sub>2</sub>-rich specimens observed in this work, suggest that the kinetics of the transformation are martensitic.

Some comments are also in order concerning the high temperature continuous solid solution between cubic UO<sub>2</sub> and tetragonal ZrO<sub>2</sub>. It is usually considered necessary for the existence of a continuous solid solution that the components have the same crystal structure. However, this does not necessarily mean identity of the crystallographic system but rather sufficient similarity of the atomic arrangements to permit random substitution. Both UO<sub>2</sub> and ZrO<sub>2</sub> have a fluorite-type structure, which in the latter case is very slightly distorted to give a tetragonal axial ratio of 1.018. Urania, being cubic, has an axial ratio of 1.000. Obviously, there is very little difference between the two structures, and since the ionic radius of U(IV) is only 12% larger than that of Zr(IV), a continuous solid solution is a reasonable expectation. This phenomenon has been observed in several other systems, listed in Table III. In all these systems, the components, although belonging to different crystallographic systems, form continuous solid solutions. However, where the structures are known in sufficient detail, it is apparent that the lattice of one component is quite similar to that of the other, a phenomenon which one might call hidden or krypto-isomorphism.

**Acknowledgments.**—The author is indebted to Professor J. E. Ricci for valuable criticism of a

preliminary report, to Mr. S. B. Austerman for suggesting the project and giving it much valuable guidance and support, to Dr. R. Chang for drawing attention to the martensitic behavior of the zirconia

TABLE III  
PAIRS OF NON-ISOMORPHOUS COMPOUNDS WHICH FORM CONTINUOUS SOLID SOLUTIONS

Compd.	Lattice types	Ref.	Compd.	Lattice types	Ref.
LiCl	FCC	18	Fe <sub>2</sub> O <sub>4</sub>	FCC	23
MgCl <sub>2</sub>	Rhombohedral	19	Mn <sub>2</sub> O <sub>4</sub>	BC tetragonal	
LiCl	FCC	20	UO <sub>2</sub>	FCC (fluorite str.)	This work
FeCl <sub>2</sub>	Rhombohedral		ZrO <sub>2</sub>	FC tetragonal (distorted fluorite structure)	
LiF	FCC				
MgF <sub>2</sub>	BC tetragonal (rutile struct.)				
UC	FCC	21	U <sub>3</sub> O <sub>8</sub>	Orthorhombic	24
UC <sub>2</sub>	FC tetragonal	22	UO <sub>3</sub>	Hexagonal	

transformation and to Messrs. T. C. Broman and V. Robling for their able assistance with many of the experiments.

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 (19) G. Bruni and A. Ferrari, *Z. Krist.*, **89**, 499 (1934).  
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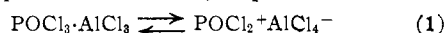
## Addition Compounds of Metal Halides with POX<sub>3</sub> Compounds

BY J. C. SHELDON AND S. Y. TYREE

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The P-O band in the infrared spectra of solid addition compounds between phosphoryl halides and metal halides is shown to shift to a lower frequency with respect to the pure phosphoryl halide. The shift is interpreted as suggesting that the bonding in the addition compounds is through oxygen. Triphenylphosphine oxide-metal halide addition compounds have been synthesized as models for comparison in which the bonding can be only through oxygen. Phase studies are reported for the systems TiBr<sub>4</sub>-PBr<sub>3</sub>, POBr<sub>3</sub>-SnBr<sub>4</sub>, POCl<sub>3</sub>-SnCl<sub>4</sub>.

In recent years a series of crystalline addition compounds of phosphoryl halides with anhydrous metal halides has been reported, notably by Gutmann.<sup>1</sup> The bonding has been regarded as due to halogen-bridge formation, using one of the halogen atoms in the phosphorus compound. Whether or not the crystalline addition compounds are regarded as covalent, it also has been postulated that the compounds ionize upon melting or upon dissolution in polar solvents,<sup>1,2</sup> cf. equation 1



It is true that the acid character of polyvalent metal halides in phosphoryl halide solvents<sup>3</sup> may be adequately explained by the solvo theory of acids and bases. The only direct evidence on structures of such compounds is the Raman spectrum of solid

POCl<sub>3</sub>·SbCl<sub>5</sub>,<sup>4</sup> which is interpreted to indicate the presence of SbCl<sub>6</sub><sup>-</sup> ions in the crystal. No X-ray structure determinations have been made on any of the compounds. Transport measurements and conductivity studies of the compounds, either in the liquid state or as solutes, have been offered as support for the ionic structures.<sup>5,6</sup> It is quite possible that small amounts of ions of the types POX<sub>2</sub><sup>+</sup> and MeCl<sub>n</sub><sup>-1</sup>, do exist in solutions of the addition compounds, while the crystalline addition compounds may be of essentially different structure types.

The P-O bond order in compounds of the type X<sub>2</sub>P=O<sup>+</sup> MeX<sub>n</sub><sup>-1</sup>, would be greater than that in compounds of the type X<sub>3</sub>P<sup>+</sup>->O<sup>-</sup>, which in turn

(1) V. Gutmann, *Z. anorg. allgem. Chem.*, **269**, 279 (1952).

(2) N. N. Greenwood and K. Wade, *J. Chem. Soc.*, 1516 (1957).

(3) J. P. McReynolds, *J. Chem. Educ.*, **17**, 116 (1940).

(4) A. Maschka, V. Gutmann and R. Sponer, *Monatsh.*, **86**, 52 (1955).

(5) V. Gutmann and R. Himml, *Z. physik. Chem. N. F.*, **4**, 157 (1955).

(6) V. Gutmann, *Z. anorg. allgem. Chem.*, **270**, 179 (1952).

would be greater than that in compounds of the type  $X_3P^+ \rightarrow O^-MeX_n$ . Consequently an infrared study of the crystalline addition compounds was undertaken by us.<sup>7</sup> Comparisons of the P-O band in an addition compound with the P-O band in the free phosphoryl halide should show a shift to lower frequencies if the oxygen serves as donor or to higher frequencies if the halogen serves as donor. Phosphine oxide addition compounds of the same type were prepared for comparison, since it is clear that only the oxygen atom can function as donor in such cases.

During the course of the research it was found that some confusion exists in the literature concerning the existence of some of the compounds we intended to use in the study. Accordingly, the systems  $PBr_3-TiBr_4$ ,  $POBr_3-SnBr_4$  and  $POCl_3-SnCl_4$  were studied by the freezing point technique.

### Experimental

**Preparation of compounds** (compounds marked\* are not reported elsewhere in the literature).  $TiCl_4 \cdot 2POCl_3$ ,  $TiCl_4 \cdot POCl_3$  and  $SnCl_4 \cdot 2POCl_3$ .—These rather well-known compounds were prepared by the mixing of the components in the appropriate molecular ratio, melting the mixture, stirring and crystallizing.

$TiBr_4 \cdot 2POBr_3$ .—The crude compound was prepared by melting the components together, followed by cooling to crystallize. It is purified by sublimation at 120° and 5 mm. The dark red, almost black, crystals melt at 187–190°.

*Anal.* Calcd. for  $TiBr_4 \cdot 2POBr_3$ : Br, 84.9; P, 6.6. Found: Br, 84.0; P, 6.45.

$FeBr_3 \cdot 2POBr_3$ \*.—The compound was prepared routinely by reacting iron(III) bromide (*cf.* (below) with boiling phosphoryl bromide, the excess  $POBr_3$  being washed away with dry cyclohexane. A well-crystallized product was obtained by the procedure of adding  $POBr_3$  to a solution of iron(III) bromide in nitrobenzene (*cf.* below). The red hexagonal platelets melt at 217–218° and cannot be sublimed without decomposition.

*Anal.* Calcd. for  $FeBr_3 \cdot 2POBr_3$ : Br, 81.0; P, 7.85; Fe, 7.1. Found: Br, 81.1; P, 7.65; Fe, 6.95.

All of the above addition compounds are hygroscopic.

**Nitrobenzene Solution of  $FeBr_3$** .—Several attempts to prepare iron(III) bromide by direct synthesis<sup>8</sup> yielded products whose stoichiometry varied from  $FeBr_{2.12}$  to  $FeBr_{2.35}$ ; yet the products all appeared to be well-crystallized single substances under the microscope. The crystals are partially soluble in nitrobenzene. The insoluble residue is iron(II) bromide. Cryoscopic measurements on the nitrobenzene solution indicated that the molecular weight of the solute iron bromide was 585.  $Fe_2Br_6$  requires 592.

$TiCl_4 \cdot 2(C_6H_5)_3PO$ \*.—Triphenylphosphine oxide was dissolved in hot, excess titanium tetrachloride. The excess  $TiCl_4$  was pumped off, leaving the orange addition compound, which was sublimed at 250° and 5 mm., m.p. 340–350°.

*Anal.* Calcd. for  $TiCl_4 \cdot 2(C_6H_5)_3PO$ : Cl, 19.0; C, 57.8; H, 4.01. Found: Cl, 18.8; C, 58.1; H, 4.22.

$Y \cdot 2(C_6H_5)_3PO$ , where  $Y = SnCl_4^*$ ,  $SnBr_4^*$  and  $FeBr_3^*$ .—These addition compounds were precipitated slowly from absolute alcoholic solutions of the appropriate components. Stirring and scratching were necessary. Anhydrous iron(II) bromide appears to be somewhat soluble in hot absolute alcohol. However the solution darkens rapidly in contact with air, presumably due to oxidation of iron(II) to iron(III). The tin tetrahalide addition compounds were prepared also by heating the triphenylphosphonium chloro- and bromostannates at 110° in air for several hours.<sup>9</sup> The tin compounds

(7) While writing this communication, we received a private communication from Dr. N. N. Greenwood stating that some unpublished infrared spectra of  $POCl_3-SnCl_4$  addition compounds exist, which corroborate that reported here.

(8) N. W. Gregory and B. A. Thackrey, *THIS JOURNAL*, **72**, 3170 (1950).

(9) J. C. Sheldon and S. Y. Tyree, *ibid.*, **80**, 2117 (1958).

can be purified by sublimation at 150° and 5 mm., but the iron compound sublimes with considerable dissociation. The  $SnCl_4$  compound forms colorless crystals, melting at 323–327°. The  $SnBr_4$  compound forms colorless crystals, melting at 283–285°. The  $FeBr_3$  compound is brown, melting at 210° with decomposition.

*Anal.* Calcd. for  $SnCl_4 \cdot 2(C_6H_5)_3PO$ : Cl, 17.4; Sn, 14.5; P, 7.6; C, 52.8; H, 3.67. Found: Cl, 17.4; Sn, 14.65; P, 7.54; C, 52.8; H, 3.65. Calcd. for  $SnBr_4 \cdot 2(C_6H_5)_3PO$ : Br, 32.1; Sn, 11.9; P, 6.25; C, 43.4; H, 3.02. Found: Br, 32.6; Sn, 12.5; P, 6.10; C, 43.6; H, 3.18. Calcd. for  $FeBr_3 \cdot 2(C_6H_5)_3PO$ : Br, 20.7; Fe, 7.25; C, 55.8; H, 3.88. Found: Br, 20.6; Fe, 7.6; C, 55.9; H, 4.08.

The triphenylphosphine oxide addition compounds are not hygroscopic.

**Freezing Point Diagrams.**—The components were weighed together and frozen. The freezing point was taken as the temperature at which solid just disappeared under conditions of very slow temperature rise. An accurate mercury thermometer was employed for temperatures as low as -38° and a standardized pentane thermometer for temperatures somewhat below this. The diagrams are given in Fig. 1.

**Infrared Spectra.**—The spectra of the solid samples were obtained in paraffin oil mulls in a Baird Associates recording spectrophotometer serial no. AB2-193. The spectral data are given in Table I. Manipulations requiring anhydrous conditions were carried out in a dry box.

### Discussion

It was once held that  $PCl_3$  and  $PBr_3$  gave addition compounds with  $TiCl_4$  and  $TiBr_4$ , respectively.<sup>10</sup> It has since been shown that no compounds are given by  $PCl_3$  and  $TiCl_4$  in the absence of oxygen and a thermal analysis of the  $POCl_3-TiCl_4$  system showed the existence of 1:1 and 2:1 addition compounds.<sup>11</sup> Thus it was concluded that the previously reported compounds were complexes of phosphoryl chloride. It was further pointed out that the same state of affairs exist in the bromide system, but no details were given at that time. Our freezing point diagram of  $PBr_3-TiBr_4$  shows a simple eutectic at 83.5 mole %  $PBr_3$ , -47°, and the compound  $(POBr_3)_2 \cdot TiBr_4$  was prepared in order to confirm the previous findings.<sup>11</sup> It is noteworthy that this is the first  $POBr_3$  addition compound reported.

There has been some confusion as to the compounds formed in the system  $POCl_3-SnCl_4$ . An early report stated that a 1:1 compound could be prepared.<sup>12</sup> Further workers doubted this and indicated that the compound formed was 2:1.<sup>13</sup> Still later workers state that the 2:1 compound probably exists, though unstable, and that a 1:1 compound also can be formed.<sup>1</sup> We find that the freezing point diagram indicates the existence of only a 2:1 compound, m.p. 55°, *cf.* m.p. 54.5°.<sup>12</sup> It is seen from the diagram that the maximum is very broad and indicates a significant degree of dissociation on melting. This may be correlated with the report<sup>13</sup> that the 2:1 compound distills at 118°, whereas the boiling points of  $POCl_3$  and  $SnCl_4$  are 107 and 114°, respectively. In the view of those authors the compound was largely dissociated in the liquid state. The freezing point diagram of the system  $POBr_3-SnBr_4$  shows only a simple eutectic at 40 mole %  $POBr_3$ , 4.5°. It

(10) M. G. Raeder, *Kgl. Norske Videnskab Selskab Skriftr.*, **3**, 1 (1929); *C. A.*, **25**, 17 (1931).

(11) W. L. Groeneveld, J. W. Spronsen and H. W. Konwenhoven, *Rec. trav. chim.*, **72**, 950 (1953).

(12) W. Casselman, *Ann.*, **91**, 242 (1854); **98**, 217 (1856).

(13) F. B. Gunner and S. Sugden, *J. Chem. Soc.*, 1298 (1929).

should be noted that no compounds were observed between  $\text{POCl}_3$  and  $\text{SnBr}_4$ .<sup>1</sup> Tin tetrahalides do not therefore appear to function as strong acceptors with the phosphoryl halides. Our qualitative tests indicate no compound of  $\text{POBr}_3$  with  $\text{ZrBr}_4$  or  $\text{AsBr}_3$ . Zirconium bromide is insoluble in boiling phosphoryl bromide and is apparently unchanged by it. This may be compared with the  $\text{POCl}_3$ - $\text{ZrCl}_4$  system which shows 1:1 and 2:1 compounds.<sup>14</sup> On contact, arsenic tribromide and phosphoryl bromide melt together with no temperature change. The corresponding chloride system,  $\text{POCl}_3$ - $\text{AsCl}_3$ , also fails to yield compounds.<sup>1</sup> Although liquid  $\text{POBr}_3$  can be seen to react with iron(II) bromide to give a 2:1 compound, boiling  $\text{POCl}_3$  appears to have scarcely any effect on iron(II) chloride. Gutmann finds  $\text{FeCl}_2$  insoluble in  $\text{POCl}_3$  also.<sup>1</sup>

The structures of solid phosphoryl halide compounds have been inferred from chemical behavior patterns. We believe that a discussion of this type of indirect evidence is unprofitable. For example, Greenwood and Wade point out that whilst  $\text{POCl}_3$  forms a compound with  $\text{BCl}_3$ , it does not with  $\text{BF}_3$ <sup>2</sup> (though it may be added that  $(\text{CH}_3)_3\text{PO}$  and  $\text{POF}_3$  in fact do form compounds with  $\text{BF}_3$ <sup>15,16</sup>) and that this would be unusual if the oxygen were used as the donor atom consistently. However, it can be seen from the data presented above that there are many apparent anomalies with regard to the existence or non-existence of phosphoryl halide compounds (*cf.* system  $\text{POCl}_3$ - $\text{FeCl}_2$ ,  $\text{POBr}_3$ - $\text{FeBr}_2$ ;  $\text{POCl}_3$ - $\text{SnCl}_4$ ,  $\text{POBr}_3$ - $\text{SnBr}_4$ ;  $\text{POCl}_3$ - $\text{ZrCl}_4$ ,  $\text{POBr}_3$ - $\text{ZrBr}_4$ ). Addition compounds of  $\text{POCl}_3$  are not restricted to metal halides, but are formed with metal oxides and hydroxides also.<sup>1</sup> In these cases the necessity of chlorine as a donor is somewhat obscure, but the strongly polar P-O group would be a suitable group for bonding to ionic metal oxygen compounds.

Several authors already have regarded the phosphoryl halide compounds as being due to coordination of the phosphoryl oxygen to the metal.<sup>13,16</sup> In view of the many solid addition compounds of phosphine oxides with metal halides,<sup>16,17</sup> there can be little doubt of the effectiveness of the phosphoryl group as a donor. The electronic structure of the phosphoryl group has been discussed and is best regarded as primarily a dative  $\sigma$ -bond from the phosphorus to the oxygen, with some  $\pi$ -bond character by back-donation of p oxygen electrons to a vacant d phosphorus orbital. It is consistent with this picture for the phosphoryl stretch frequency at about  $1300 \text{ cm.}^{-1}$  to be quite sensitive to the electro-negativity of the substituent atoms or groups on the phosphorus atom,<sup>18</sup> as a greater withdrawal of electrons from the phosphorus by such groups would encourage a

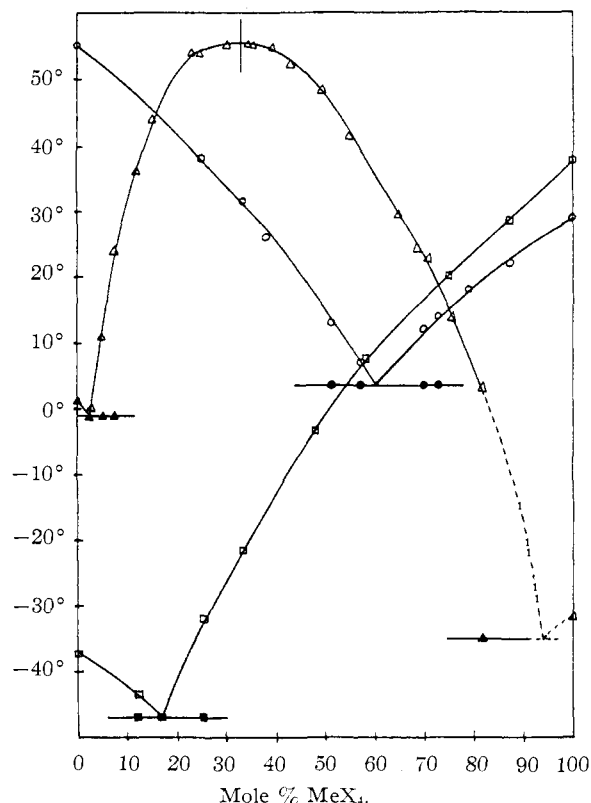


Fig. 1.— $\text{POCl}_3$ - $\text{SnCl}_4$ ,  $\triangle$ - $\triangle$ -;  $\text{POBr}_3$ - $\text{SnBr}_4$ ,  $\circ$ - $\circ$ -;  $\text{POCl}_3$ - $\text{SnCl}_4$ ,  $\square$ - $\square$ -;  $\text{POBr}_3$ - $\text{TiBr}_4$ ,  $\circ$ - $\circ$ -.

greater degree of back-donation from the oxygen to phosphorus. The bond order then increases and the frequency also. It is clear that donation of electrons by the chlorine or by the oxygen atoms of  $\text{POCl}_3$  would have opposite effects on the P-O group bond order, as the former would encourage back-donation and the latter inhibit back-donation of the oxygen electrons to the phosphorus atom.

In Table I are listed the phosphoryl frequency shifts found in the solid state for the compounds prepared in this report. In every case but  $\text{SnCl}_4 \cdot 2\text{POCl}_3$ , no band is found in the expected position for the free phosphoryl group of the appropriate donor, and a strong band is found 50 to  $95 \text{ cm.}^{-1}$  to the lower frequency side of the expected position. We believe that such a strong shift to lower frequency can only be reasonably explained by assuming that the phosphoryl oxygen is the donor entity in these complexes. There is little doubt in any event that compound formation by  $\text{Ph}_3\text{PO}$  involves the oxygen atom and it is of importance to note that the shift observed for the phosphine oxide compounds is of the same order as for the phosphoryl halide complexes.

It must be noted that the phosphoryl band is rarely shifted without some change of shape or structure in the above spectra. The PO band is reasonably sharp in pure  $\text{POCl}_3$  and  $\text{POBr}_3$ , but appears to have closely spaced fine structure in  $\text{Ph}_3\text{PO}$ . The PO bands of the  $\text{POBr}_3$  addition compounds appear relatively simple, that of  $\text{FeBr}_2 \cdot 2\text{POBr}_3$  being sharp and that of  $\text{TiBr}_4 \cdot 2\text{POBr}_3$  somewhat broad with a barely resolved shoulder

(14) E. M. Larsen, J. Howatson, A. M. Gammill and L. Wittenberg, *THIS JOURNAL*, **74**, 3489 (1952).

(15) A. B. Burg and W. E. McKee, *ibid.*, **73**, 4590 (1951).

(16) H. S. Booth and J. H. Walkup, *ibid.*, **65**, 2334 (1943).

(17) W. Reppe and W. Schweckendiek, German Patent 805,642; *C. A.*, **47**, 602 (1953); A. E. Arbuzov and K. V. Nikonov, *Zhur. Obshchei Khim.*, **18**, 2008 (1948); *C. A.*, **43**, 3801 (1949); R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, 262 (1908).

(18) J. V. Bell, J. Heisler, H. Tannenbaum and J. Goldenson, *THIS JOURNAL*, **76**, 5185 (1954).

TABLE I

Compound	Phosphoryl frequency (cm. <sup>-1</sup> )	Shift (cm. <sup>-1</sup> )
POCl <sub>3</sub>	1300 <sup>a</sup>	..
(POCl <sub>3</sub> ) <sub>2</sub> ·TiCl <sub>4</sub>	1205	95
POCl <sub>3</sub> ·TiCl <sub>4</sub>	1205	95
(POCl <sub>3</sub> ) <sub>2</sub> ·SnCl <sub>4</sub>	1215	85
	1300, 1285 <sup>b</sup>	
POBr <sub>3</sub>	1270	..
(POBr <sub>3</sub> ) <sub>2</sub> ·TiBr <sub>4</sub>	1185	85
(POBr <sub>3</sub> ) <sub>2</sub> ·FeBr <sub>2</sub>	1220	50
Ph <sub>3</sub> PO	1180	..
(Ph <sub>3</sub> PO) <sub>2</sub> ·SnCl <sub>4</sub>	1125	55
(Ph <sub>3</sub> PO) <sub>2</sub> ·SnBr <sub>4</sub>	1125	55
(Ph <sub>3</sub> PO) <sub>2</sub> ·TiCl <sub>4</sub>	1130	50
(Ph <sub>3</sub> PO) <sub>2</sub> ·FeBr <sub>2</sub>	1125	55

<sup>a</sup> Thin film of liquid. <sup>b</sup> Partially resolved doublet.

maximum on the high frequency side. The shoulder maximum is more pronounced and resolved in POCl<sub>3</sub>·TiCl<sub>4</sub> and TiCl<sub>4</sub>·2POCl<sub>3</sub> (which have identical spectra) and this is also true for the spectrum of SnCl<sub>4</sub>·2POCl<sub>3</sub>. The most notable feature of this tin(IV) chloride compound is a strong doublet at the expected free POCl<sub>3</sub> phosphoryl frequency. The area under this doublet is approximately two-thirds that of the shifted band. In consideration of the similarity in shape and position between the shifted component of the PO band in SnCl<sub>4</sub>·2POCl<sub>3</sub> and that of the shifted band in POCl<sub>3</sub>·TiCl<sub>4</sub> it must be concluded that a substantial proportion of the POCl<sub>3</sub> groups are indeed bonded to the tin in the SnCl<sub>4</sub> compound. The unchanged component may represent the absorption of a portion of the POCl<sub>3</sub> molecules in the crystal that are temporarily not bonded but nevertheless

remain localized due to other crystal forces. The instability of this compound already has been mentioned and dissociation may well be prevalent within the crystal at temperatures 35° below its m.p., the temperature at which the spectrum was obtained.

The shifted PO bands of the SnBr<sub>4</sub> and TiBr<sub>4</sub> compounds of Ph<sub>3</sub>PO do not reveal much fine structure, but those of the SnCl<sub>4</sub> and FeBr<sub>2</sub> compounds are clearly resolved into three submaxima. The frequencies given in Table I refer to that of the maximum in the proposed PO absorption band when more than one peak is detectable in the band envelope. There are two very strong absorption bands in the spectrum of Ph<sub>3</sub>PO in the 1200 to 1100 cm.<sup>-1</sup> region and both are shifted to relatively the same extent.

In preliminary studies, we have found that the addition compounds of aluminum chloride with thionyl chloride<sup>19</sup> and benzoyl chloride<sup>20</sup> also show thionyl and carbonyl bands shifted to lower frequency by about 115 and 45 cm.<sup>-1</sup>, respectively. This may be compared with the shift to higher frequency that nitrosyl chloride undergoes on complex formation with aluminum chloride. This complex is undoubtedly of the structure NO<sup>+</sup>·AlCl<sub>4</sub><sup>-</sup> and the nitrosyl frequency in this solid compound is 2236 cm.<sup>-1</sup> compared with the NO frequency of 1800 cm.<sup>-1</sup> in pure nitrosyl chloride.<sup>21</sup>

**Acknowledgment.**—This work was supported in part by the Office of Naval Research.

(19) H. Hecht, *Z. anorg. Chem.*, **254**, 37 (1947)

(20) B. Menshutkin, *J. Russ. Phys. Chem. Soc.*, **42**, 1310 (1910); *Chem. Zentr.*, **82**, 11, 481 (1911).

(21) H. Gerding and H. Hontgraaf, *Rec. trav. chim.*, **72**, 21 (1953).  
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## The Exchange of Oxygen between Phosphoric Acid and Water<sup>1</sup>

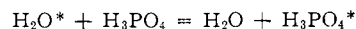
BY BERNARD KEISCH,<sup>2</sup> JOSEPH W. KENNEDY<sup>3</sup> AND ARTHUR C. WAHL

RECEIVED MAY 10, 1958

The kinetics of the exchange of isotopic oxygen between phosphoric acid and water has been studied. The rate of exchange increases rapidly with the phosphoric acid concentration, the half-time of exchange at 100° decreasing from 250 hour at 5.9 *f* H<sub>3</sub>PO<sub>4</sub> to 0.20 hour at 18.3 *f* H<sub>3</sub>PO<sub>4</sub>. The observed rate may be expressed as a function of the H<sub>2</sub>O and H<sub>3</sub>PO<sub>4</sub> activities *a<sub>w</sub>* and *a<sub>1</sub>*, respectively, in the following manner: rate = *k*<sub>1</sub>*a*<sub>1</sub>*a<sub>w</sub>* + *k*<sub>2</sub>*a*<sub>1</sub><sup>2</sup> + *k*<sub>3</sub>*a*<sub>1</sub><sup>3</sup>/*a<sub>w</sub>*. The first term is of primary importance at the lower phosphoric acid concentrations, and the second term is the important one at the higher concentrations. The third term contributes appreciably (~10%) only in the most concentrated solutions. The proposed mechanism involves direct replacement of oxygen in H<sub>3</sub>PO<sub>4</sub> (first term) and the reversible formation and hydrolysis of H<sub>4</sub>P<sub>2</sub>O<sub>7</sub> and H<sub>5</sub>P<sub>3</sub>O<sub>10</sub> (second and third terms). Support for exchange *via* reversible formation and hydrolysis of H<sub>4</sub>P<sub>2</sub>O<sub>7</sub> is given by the equivalence of the exchange rate and the rate of H<sub>4</sub>P<sub>2</sub>O<sub>7</sub> hydrolysis in the concentrated solutions. The activation energy measured at various concentrations of phosphoric acid decreases from 26.5 kcal./mole at 8.8 *f* H<sub>3</sub>PO<sub>4</sub> to 19.7 kcal./mole at 17.8 *f* H<sub>3</sub>PO<sub>4</sub>.

The exchange of oxygen between water and phosphoric acid or its salts has been studied qualitatively by a number of workers.<sup>4-8</sup> Some of the

results are contradictory. This paper describes a detailed study of the kinetics of the reaction



We have measured the rate of the exchange as a function of the acid concentration and also the rate of hydrolysis of pyrophosphoric acid in concentrated phosphoric acid solutions. We have at-

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(2) Phillips Petroleum Fellow, 1955-1957.

(3) Deceased, May 5, 1957.

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