

[DIVISION OF CHEMICAL DEVELOPMENT, TENNESSEE VALLEY AUTHORITY]

## Structure of Crystalline Phosphoric Acid

BY JAMES P. SMITH, WALTER E. BROWN AND JAMES R. LEHR

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The crystal structure of anhydrous orthophosphoric acid was determined by means of two-dimensional Fourier projections. The unit cell dimensions are  $a = 5.80 \pm 0.02$ ,  $b = 4.85 \pm 0.02$ ,  $c = 11.62 \pm 0.04$  Å., and angle  $\beta = 95^\circ 20' \pm 20'$ . The space group is  $C_{2h}^5 - P2_1/c$  with four formula weights of  $H_3PO_4$  per unit cell. The lattice constants of orthophosphoric acid hemihydrate are  $a = 7.94 \pm 0.04$ ,  $b = 12.94 \pm 0.02$ ,  $c = 7.38 \pm 0.02$  Å., and angle  $\beta = 109^\circ 25' \pm 30'$ . The space group is  $C_{2h}^5 - P2_1/a$  with four formula weights of  $2H_3PO_4 \cdot H_2O$  per unit cell. The optical and morphological properties of the two crystalline forms of the acid are given.

Orthophosphoric acid crystallizes as the anhydrous acid ( $H_3PO_4$ , m.p.  $+2.4^\circ$ ) and as the hemihydrate ( $2H_3PO_4 \cdot H_2O$ , m.p.  $29.3^\circ$ ). Little has been reported on the crystallography of either. The unit cell dimensions and space group for the anhydrous acid were reported by Furberg<sup>1</sup> in a recent note. He also gave a preliminary electron density projection along the  $b$ -axis but did not give atomic parameters. The morphological, optical and X-ray properties of the two crystalline forms of the acid are described here. The structure of the anhydrous acid is presented in detail.

## Materials and Methods

Anhydrous phosphoric acid was triply crystallized by the method of Ross and Jones.<sup>2</sup> The hemihydrate was triply crystallized from reagent-grade phosphoric acid.

The reactivity of the crystals complicated measurements of their refractive indexes. Hydrocarbon oils, freed of water and reactive impurities by treatment with solid phosphoric oxide, were recalibrated and used immediately. The refractive indexes were measured with white light at room temperature and at temperatures below the ice point. The oil calibrations were checked to  $0^\circ$  against solid immersion media. The index measurements for the crystals were corrected to  $25^\circ$ . The relative magnitudes of the indexes were verified by independent measurements of birefringence on principal sections and by a comparison of the calculated optic angle  $2V$  with measured values obtained by Mallard's method.

The Weissenberg camera was 57.3 mm. in diameter. Lattice constants were determined with  $CuK\alpha$  radiation ( $\lambda = 1.54$  Å.).

**Anhydrous Phosphoric Acid. Morphological and Optical Properties.**—Anhydrous phosphoric acid crystallizes as colorless, euhedral, prismatic crystals belonging to the monoclinic system, holohedral class. The prism comprises nearly equally developed  $b$ -zone forms  $\{100\}$ ,  $\{001\}$  and  $\{102\}$ , with termination forms  $\{120\}$ ,  $\{012\}$  and sometimes  $\{010\}$ . Rapid growth produces acicular crystals elongated parallel to the  $b$ -axis. Tubular crystals are common. No cleavage was found. Polysynthetic twinning occurs on  $(100)$ .

The refractive indexes are  $\alpha = 1.455$ ,  $\beta = 1.504$  and  $\gamma = 1.505$ . Birefringence is extreme, with  $\gamma - \alpha = 0.050$ . The crystals are biaxial ( $-$ ). The optic axial plane is  $(010)$ , with  $Bx_a$  (or  $X$ ) inclined to  $a$  by  $23^\circ$  in acute beta and  $Z$  inclined to  $c$  by  $28^\circ$  in obtuse beta. Monoclinic angle  $\beta = 95^\circ 30'$ . The optic axial angle  $2V$ , as determined by Mallard's method, is  $9^\circ 32'$  at  $610 m\mu$ ,  $13^\circ 38'$  at  $425 m\mu$  and  $12^\circ 16'$  with white light. Dispersion is weak, with  $v > r$ . The nearly isotropic  $\gamma - \beta$  crystal section, when viewed down the  $Bx_a$ , shows an anomalous interference color, Berlin blue.

(1) S. Furberg, *Acta Chem. Scand.*, **8**, 532 (1954).(2) W. H. Ross and R. M. Jones, *This Journal*, **47**, 2165 (1925).

**Determination of the Structure.**—The unit cell dimensions, as obtained from rotation and Weissenberg photographs about the  $a$ - and  $b$ -axes are  $a = 5.80 \pm 0.02$  Å.;  $b = 4.85 \pm 0.02$  Å.;  $c = 11.62 \pm 0.04$  Å.; angle  $\beta = 95^\circ 20' \pm 20'$ . These agree, within the specified limits of error, with the measurements reported by Furberg<sup>1</sup> ( $a = 5.78$  Å.;  $b = 4.84$  Å.;  $c = 11.65$  Å.;  $\beta = 95^\circ 30'$ ).

The density of crystalline phosphoric acid has not been measured. A density of  $1.874$  g.  $cm.^{-3}$  is reported<sup>3</sup> for liquid (100%) phosphoric acid at  $25^\circ$ . An assumption that the unit cell contains four formula weights leads to a density of  $1.99$  g.  $cm.^{-3}$  for the crystalline acid. The calculated density agrees satisfactorily with the density of liquid phosphoric acid when the contraction of the liquid upon freezing is taken into account.

Two systematic extinctions were observed— $h0l$  with  $l$  odd and  $0k0$  with  $k$  odd. The space group is therefore  $C_{2h}^5 - P2_1/c$ , as reported by Furberg,<sup>1</sup> and the asymmetric unit is one molecule of anhydrous phosphoric acid.

Intensities were estimated visually from zero-layer Weissenberg photographs taken with  $MoK\alpha$  radiation. No reflections were observed at values of  $\sin \theta/\lambda$  greater than 0.75. The multiple-film technique was used, three films being interleaved with nickel foil. The intensities were corrected for Lorentz and polarization factors.<sup>4</sup> Corrections for absorption were made graphically.<sup>5</sup> No correction was made for extinction or spot size. Variation in spot size is regarded as the major source of error in the observed structure factors. The dimensions of the crystals were 0.45 by 0.31 by 3.0 mm. for the  $a$ -axis setting and 0.26 by 0.46 by 3.5 mm. for the  $b$ -axis setting.

For this space group, the small  $b$ -dimension of the unit cell is evidence against an overlap of phosphate tetrahedra in the  $b$ -direction. A preliminary picture of the structure therefore was obtained from  $(010)$  projections. The positions of the phosphorus atoms were derived first from a Patterson projection. Various tentative structures were evaluated by optical diffraction methods<sup>6</sup> with an apparatus similar in design and dimensions to one described by Buerger.<sup>7</sup> The approximate structure so obtained was checked by means of an optical Fourier synthesis in which the phase shifters were cast collodion films instead of mica sheets.<sup>7</sup>

(3) E. P. Egan, Jr., and B. B. Luff, *Ind. Eng. Chem.*, in press.(4) M. J. Buerger and G. E. Klein, *J. Appl. Phys.*, **16**, 408 (1945).(5) G. Albrecht, *Rev. Sci. Instr.*, **10**, 221 (1939).(6) A. W. Hanson, *Acta Cryst.*, **6**, 35 (1953).(7) M. J. Buerger, *J. Appl. Phys.*, **21**, 909 (1950).

The structure was refined manually in three successive two-dimensional Fourier syntheses. The  $x$ - and  $z$ -parameters of three oxygen atoms and the phosphorus atom were selected from the final Fourier projection. Since the fourth oxygen atom was poorly resolved from the phosphorus atom, the parameters of  $O_4$  were varied to obtain the best agreement between observed and calculated structure factors. The resulting atomic coordinates are shown in Table I. With these coordinates and a temperature factor,  $\exp[-B(\sin\theta/\lambda)^2]$ , structure factors were calculated. A thermal parameter,  $B$ , of  $1.6 \text{ \AA}^2$  gave the best agreement between observed and calculated values. The  $(h0l)$  structure factors are available.<sup>8</sup>

The reliability index,  $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ , is 0.20 with the unobserved reflections neglected and is 0.21 with the unobserved  $F$ 's included at half the minimum observable amplitude.

With the  $x$  and  $z$ -parameters known, an assumption that the phosphate group formed a regular tetrahedron with a P-O distance of  $1.56 \text{ \AA}$ . made possible the calculation of tentative  $y$ -parameters for the oxygen atoms relative to the phosphorus atom as the origin. The structure factors thus could be calculated as functions of a single parameter—the position of the phosphorus atom along the  $b$ -axis. Structure factors of four reflections (020, 040, 060 and 011) were plotted for values of this single parameter between zero and one-half. A comparison of the observed amplitudes with the plot showed that this parameter for the phosphorus atom must be near 0.30. The reliability index for the  $0kl$  series calculated from these tentative parameters was 0.29.

The  $y$ - and  $z$ -parameters were refined in three successive two-dimensional Fourier syntheses. Because of poor resolution, it was necessary to vary the  $y$ -parameter of an oxygen atom,  $O_2$ , until the best agreement between calculated and observed structure factors was reached. The atomic coordinates are shown in Table I. With a thermal parameter,  $B$ , of  $1.6 \text{ \AA}^2$ , the reliability index,  $R$ , for the  $0kl$  series of reflections is 0.18 when the unobserved reflections are neglected and is 0.21 when the unobserved  $F$ 's are included at half the minimum observable amplitude. The calculated and observed structure factors for the  $a$ -axis projection are available.<sup>8</sup>

TABLE I

ATOMIC COORDINATES OF ANHYDROUS PHOSPHORIC ACID

Atom	$x$	$y$	$z$
$O_1$	0.264	0.132	0.035
$O_2$	-.052	.310	.122
$O_3$	.288	.150	.255
$O_4$	.320	.610	.133
P	.210	.310	.140

**Description of Structure.**—Three points of evidence support the general features of the structure

(8) Amplitude data for the 78 observed and 26 unobserved  $h0l$  reflections and for the 46 observed and 24 unobserved  $0kl$  reflections have been deposited as Document number 4471 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 \$1.25 for photoprints or \$1.25 for 35-mm. microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

reported here: (1) The reliability indexes for the two projections are in the range usually set for a correct structure, and there are no major discrepancies between the individual calculated and observed structure factors; (2) the relatively small index of reliability (0.29) for the tentative  $a$ -axis projection serves as an independent check of the  $x$ - and  $z$ -parameters; (3) Furberg's<sup>1</sup> electron density map supports the present conclusions as to position and orientation of the phosphate unit.

The distances between atoms of a given tetrahedron, as calculated from the parameters in Table I, are listed in Table II. The average P-O distance,  $1.56 \text{ \AA}$ ., is the same as that reported by West<sup>9</sup> for  $\text{KH}_2\text{PO}_4$ . The deviations from this value in Table II probably are not significant.

TABLE II

DISTANCES BETWEEN ATOMS OF A PHOSPHATE TETRAHEDRON,  $\text{\AA}$ .

P-O <sub>1</sub> = 1.55	O <sub>1</sub> -O <sub>2</sub> = 2.34
P-O <sub>2</sub> = 1.52	O <sub>1</sub> -O <sub>3</sub> = 2.55
P-O <sub>3</sub> = 1.57	O <sub>1</sub> -O <sub>4</sub> = 2.59
P-O <sub>4</sub> = 1.59	O <sub>2</sub> -O <sub>3</sub> = 2.51
	O <sub>2</sub> -O <sub>4</sub> = 2.60
	O <sub>3</sub> -O <sub>4</sub> = 2.66

The comparatively short  $O_1$ - $O_2$  distance suggests a distortion of the  $\text{PO}_4$  tetrahedron. Furberg's<sup>1</sup> tentative results also indicate a relatively short  $O_1$ - $O_2$  distance when it is assumed that the  $y$ -parameters he finds for these atoms will agree fairly well with the present ones. Electrostatic considerations indicate an improbability that the apparent shortening of the  $O_1$ - $O_2$  distance is caused by an intramolecular hydrogen bond.

The distances between oxygen atoms of adjacent tetrahedra are shown in Table III. The two pairs of interatomic distances designated A and B in Table III are taken as hydrogen bonds in accordance with the usual assumption that hydrogen bonds are indicated by short O-O distances. The third pair of hydrogen bonds can be assigned with less certainty. Entry C in Table III appears to be the most probable pair because of its length. Hydrogen bonds A and B are shown in Fig. 1, and the suggested hydrogen bond pair C can be visualized between  $O_4$  of the reference tetrahedron and  $O_1$  of the tetrahedron related by an upward  $b$ -translation.

TABLE III

DISTANCES BETWEEN OXYGEN ATOMS OF ADJACENT PHOSPHATE TETRAHEDRA,  $\text{\AA}$ .<sup>a</sup>

A	$O_4$ - $O_3$ III <sup>b</sup> = 2.52	D	$O_4$ - $O_3$ IV = 2.99
	$O_3$ - $O_4$ VII		$O_3$ - $O_4$ V
B	$O_2$ - $O_3$ II = 2.65	E	$O_2$ - $O_1$ I = 3.00
	$O_3$ - $O_2$ VI		$O_1$ - $O_2$ I
C	$O_1$ - $O_4$ V = 2.78		
	$O_4$ - $O_1$ IV		

<sup>a</sup> All other distances were greater than  $3 \text{ \AA}$ . <sup>b</sup> The Roman numerals designate phosphate groups surrounding the reference tetrahedron in Fig. 1: IV = ref. +  $\bar{b}$ ; V = ref. -  $\bar{b}$ ; VI = II -  $\bar{b}$ ; VII = III -  $\bar{b}$ .

The first two pairs of hydrogen bonds tie the phosphate units into layers parallel to the  $c$ -face,

(9) J. West, *Z. Krist.*, **74**, 306 (1930).

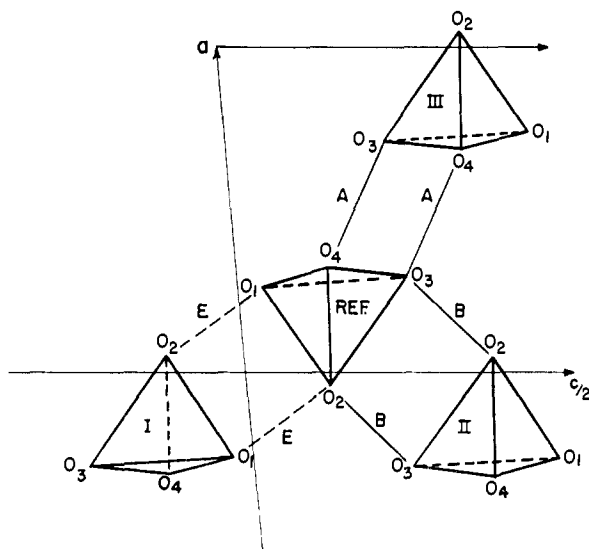


Fig. 1.—Arrangement of phosphate tetrahedra in the  $b$ -axis projection of  $\text{H}_3\text{PO}_4$ .

with two layers per unit cell. The hydrogen bond pair C would further tie together the phosphate units within each layer. Such a structure should have a plane of weakness parallel to the  $c$ -face. Attempts to demonstrate a cleavage plane on well-formed microscopic crystals were unsuccessful. Of the remaining alternatives, D of Table III would not change the layer-like nature of the structure, whereas E would tie the layers together into a three-dimensional network. Furberg<sup>1</sup> indicated a choice of hydrogen bonds corresponding to A, B and E, but since he did not give interatomic distances his choice cannot be evaluated.

Once the positions of six hydrogen bonds are known, the locations of the hydrogen atoms within the bonds can be postulated. If the selection of hydrogen bonds A, B and C is correct,  $\text{O}_1$  and  $\text{O}_2$  participate in one hydrogen bond each, whereas  $\text{O}_3$  and  $\text{O}_4$  participate in two hydrogen bonds each. The hydrogen atoms can reasonably be expected to reside closer to the "singly bonded" oxygens,  $\text{O}_1$  and  $\text{O}_2$ , than to the "doubly bonded" oxygens,  $\text{O}_3$  and  $\text{O}_4$ . In the sense suggested by Bernal and Megaw,<sup>10</sup> bond pairs B and C would be "hydroxyl" bonds, and pair A could be a "hydrogen" bond. The bond distances are in accord with this because A is shorter than B and C.

(10) J. D. Bernal and H. D. Megaw, *Proc. Roy. Soc. (London)*, **A151** 384 (1935).

The uncertainties regarding the short  $\text{O}_1$ - $\text{O}_2$  distance and the position of the third hydrogen bond each involve one atom whose parameters were not clearly resolved in the electron density projections. A further refinement of the structure from the present intensity data would not remove these uncertainties. A refinement based upon more precise intensities and a larger number of reflections appears to be warranted.

**Phosphoric Acid Hemihydrate. Morphological and Optical Properties.**—Phosphoric acid hemihydrate crystallizes as colorless, euhedral, tabular and rod-like crystals belonging to the monoclinic system, holohedral class. Rapid growth produces (001) tabular crystals showing marked elongation parallel to the  $a$ -axis. The  $a$ -zone forms are  $\{021\}$ ,  $\{001\}$  and  $\{010\}$ . The rods are terminated by a prominent  $\{120\}$  form and less prominent  $\{1\bar{2}1\}$ ,  $\{324\}$  and  $\{201\}$  forms. Merohedral crystals are common. Twinning was not observed. There is an imperfect cleavage parallel to (010). The crystals shatter internally when cooled suddenly.

The refractive indexes are  $\alpha = 1.485$ ,  $\beta = 1.492$  and  $\gamma = 1.519$ . Birefringence is strong, with  $\gamma - \alpha = 0.034$ . The crystals are biaxial (+). The optic axial plane is (010). Monoclinic angle  $\beta = 109^\circ$ . Extinction angles are  $Z\Lambda a = 20^\circ$  in acute beta and  $X\Lambda c = 39^\circ$  in obtuse beta. The optic axial angle  $2V$  is  $56^\circ \pm 2^\circ$  as determined by Mallard's method and  $54^\circ 58'$  as calculated from refractive indexes. Dispersion is very weak with  $r > v$ .

**X-Ray Measurements.**—In thin-walled capillaries the crystals grew with the  $a$ -axis parallel to the capillary. All the X-ray data therefore were obtained from a single orientation. A rotation photograph and zero-, first-, second- and third-layer Weissenberg photographs were made. A composite zero- and second-layer Weissenberg photograph was made for determination of angle  $\beta$ .

The dimensions of the unit cell are  $a = 7.94 \pm 0.04$ ;  $b = 12.94 \pm 0.02$ ;  $c = 7.38 \pm 0.02\text{\AA}$ ; and angle  $\beta = 109^\circ 25' \pm 30'$ .

Two extinctions were observed— $h0l$  with  $h$  odd and  $0k0$  with  $k$  odd. The space group is  $C_{2h}^5\text{-P}2_1/a$ . The calculated density with four formula weights of  $2\text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O}$  per unit cell is  $1.98 \text{ g. cm.}^{-3}$ . A density of  $1.770 \text{ g. cm.}^{-3}$  at  $25^\circ$  is reported<sup>3</sup> for the liquid of corresponding composition.

Although the two crystalline forms of phosphoric acid have the same space-group symmetry, no structural similarity is evident from the dimensions of the respective unit cells.

WILSON DAM, ALABAMA