

## STUDY OF X-RAY POWDER DIFFRACTION AND INFRARED ABSORPTION OF $P_2O_5$ (O'-FORM)

SIDDIQUE AHMED\*

*The Institute for Silicate Research and the Institute for Inorganic Chemistry,  
Chalmers University of Technology, Gothenburg, Sweden*

(Received May 22, 1970)

X-ray powder diffraction data of the stable orthorhombic form (O'-form) of phosphorus pentoxide have been indexed. IR spectra of both the hexagonal (H-form) and the O'-form have been recorded.

Phosphorus pentoxide exists in different modifications both in the crystalline and in the amorphous state. Commercial  $P_2O_5$  is hexagonal and is known as the H-form. It can be obtained in the pure state by resublimation *in vacuo*. A powdery amorphous type of  $P_2O_5$  may be obtained by rapid cooling during sublimation. There are two orthorhombic forms, one is metastable (O-form) and the other stable (O'-form). The stable form was prepared and used as a reagent during the investigation of the systems  $MgO-P_2O_5$  and  $Cr_2O_3-P_2O_5$  by the author. Its X-ray powder diffraction data were not indexed previously. Hill, Faust and Hendricks<sup>1</sup> say that if the orthorhombic form is heated below its melting point (569°C) for a long time a tetragonal (T-form) modification of  $P_2O_5$  is produced. They have recorded its X-ray powder diffraction data.

### Experimental

Certain amount (*ca.* 3 g) of commercial  $P_2O_5$  was sealed in a Pyrex glass tube. The tube was evacuated during sealing. It was then heated at 400°C for 6 hr in a platinum-rhodium wire wound tube furnace. After cooling to the room temperature the glass tube was cut-opened in a dry-box made for handling hygroscopic materials. Phosphorus pentoxide formed a hard mass. It was transferred to an air-tight reagent bottle and preserved in a desiccator containing  $P_2O_5$  as desiccating agent. This sample was used for X-ray and IR analyses.

The X-ray powder diffractogram of the stable orthorhombic form of  $P_2O_5$  was recorded with the help of a Philips X-ray diffractometer using copper target and nickel filter. The scanning speed was 0.5°/min. The samples for X-ray analyses were prepared in a dry-box. The hard mass of  $P_2O_5$  was powdered finely in an agate mortar and then put into the cavity of the sample holder; it was immediately covered with a transparent tape to prevent absorption of moisture by

the sample. The tape itself shows no X-ray diffraction, so it created no trouble during X-ray analyses. The IR spectra of both the H-form and the O'-form were recorded by KBr tablet method on a Beckman spectrophotometer model IR9.

### Results and Discussions

X-ray powder diffraction data of the stable orthorhombic form of  $P_2O_5$  have been shown in Table 1. The *d*-values (interplanar spacings) in this table are quite different from that of the H-form (Table 2) and the T-form (Table 3) of  $P_2O_5$ . It shows that the O'-form is a new phase.

The transformation of the hexagonal  $P_2O_5$  to the stable orthorhombic form occurs at 400°C and the process of change is sluggish. The density of the hexagonal form is 2.10 g/cm<sup>3</sup> while that of the orthorhombic form is 1.87 g/cm<sup>3</sup>. This shows that the structure of the O'-form is more open and as a result the volume of its unit cell is bigger. The IR spectrum (Fig. 1a) of the orthorhombic form contains several well-defined absorption bands which supports that there are substantial amount of vibrations among the atoms and there are bendings of the bonds in the  $P_2O_5$  molecule. All the absorption bands lie in the region 1400 cm<sup>-1</sup> to 400 cm<sup>-1</sup>. The two bands at 825 cm<sup>-1</sup> and 800 cm<sup>-1</sup> respectively are very sharp. The IR spectrum (Fig. 1b) of the hexagonal form of  $P_2O_5$  is quite different. It contains no well-defined absorption bands. There is one strong and broad valley in the wavelength range 3200 cm<sup>-1</sup> to 2600 cm<sup>-1</sup>. There is another similar valley in the wavelength range 1350 cm<sup>-1</sup> to 800 cm<sup>-1</sup>; in this region there are two absorption bands of medium intensities. The absorption band at 470 cm<sup>-1</sup> is very strong but broad. This spectrum (1b) shows all the characteristics of the hexagonal structure of the H-form of  $P_2O_5$ .

The structure of  $P_2O_5$  is complex. The stable orthorhombic form consists of an infinite array of  $PO_4$  tetrahedra.<sup>2</sup> Each of the tetrahedra shares three of its oxygen atoms with other  $PO_4$

\*Now at Glass and Ceramics Research Division, PCSIR Laboratories, Dacca 5.

TABLE 1.—X-RAY POWDER DIFFRACTION DATA FOR  $P_2O_5$  (O'-FORM).

| $d\text{\AA}$ | $I/I_1$ | $d\text{\AA}$ | $I/I_1$ | $d\text{\AA}$ | $I/I_1$ |
|---------------|---------|---------------|---------|---------------|---------|
| 4.2400        | 100     | 1.4880        | 3       | 1.1937        | 2       |
| 4.0490        | 6       | 1.4650        | 1       | 1.1875        | 1       |
| 3.6160        | 5       | 1.4466        | 5       | 1.1780        | 5       |
| 3.4250        | 16      | 1.4446        | 3       | 1.1750        | 2       |
| 3.1000        | 2       | 1.4338        | 1       | 1.1703        | 2       |
| 2.8625        | 41      | 1.4192        | 10      | 1.1674        | 1       |
| 2.7340        | 2       | 1.4154        | 4       | 1.1577        | 1       |
| 2.6180        | 19      | 1.3986        | 2       | 1.1427        | 1       |
| 2.3710        | 33      | 1.3964        | 1       | 1.1410        | 1       |
| 2.3380        | 36      | 1.3820        | 1       | 1.1199        | 2       |
| 2.2040        | 14      | 1.3423        | 1       | 1.1067        | 2       |
| 2.0580        | 2       | 1.3115        | 4       | 1.1048        | 1       |
| 2.0255        | 29      | 1.3085        | 2       | 1.0680        | 1       |
| 1.9386        | 20      | 1.2707        | 3       | 1.0663        | 1       |
| 1.9330        | 20      | 1.2664        | 1       | 1.0553        | 1       |
| 1.8860        | 1       | 1.2613        | 3       | 1.0448        | 1       |
| 1.8156        | 5       | 1.2592        | 1       | 1.0418        | 1       |
| 1.7124        | 1       | 1.2452        | 1       | 1.0355        | 1       |
| 1.7026        | 1       | 1.2431        | 1       | 1.0130        | 2       |
| 1.6750        | 8       | 1.2222        | 9       | 1.0095        | 2       |
| 1.6246        | 1       | 1.2190        | 4       | 0.9843        | 1       |
| 1.5418        | 2       | 1.2106        | 2       | 0.9755        | 2       |
| 1.5178        | 9       | 1.2068        | 2       | 0.9725        | 1       |
| 1.5120        | 3       | 1.2023        | 2       | 0.9705        | 1       |
| 1.4944        | 8       | 1.1974        | 5       | 0.9651        | 1       |

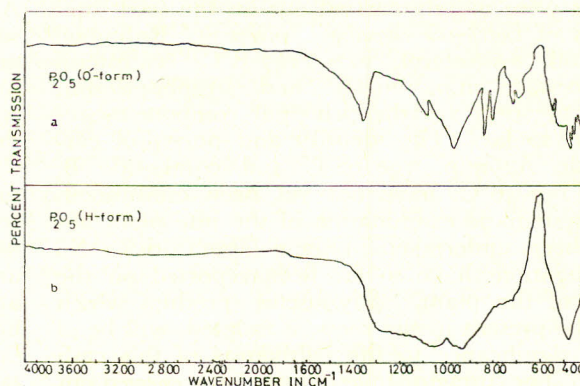
TABLE 2.—X-RAY POWDER DIFFRACTION DATA FOR  $P_2O_5$  (H-FORM).<sup>3</sup>

| $d\text{\AA}$ | $I/I_1$ | $d\text{\AA}$ | $I/I_1$ | $d\text{\AA}$ | $I/I_1$ |
|---------------|---------|---------------|---------|---------------|---------|
| 5.4000        | 100     | 1.7900        | 3       | 1.2500        | 3       |
| 5.2000        | 53      | 1.7500        | 1       | 1.2400        | 3       |
| 3.7200        | 4       | 1.6900        | 1       | 1.2100        | 1       |
| 3.3900        | 11      | 1.6700        | 2       | 1.1900        | 3       |
| 3.2700        | 33      | 1.6300        | 1       | 1.1600        | 1       |
| 3.1500        | 20      | 1.5900        | 1       | 1.1400        | 1       |
| 3.0200        | 53      | 1.5600        | 1       | 1.1300        | 2       |
| 2.5700        | 8       | 1.5200        | 4       | 1.1000        | 1       |
| 2.4300        | 17      | 1.4900        | 5       | 1.0900        | 1       |
| 2.3200        | 8       | 1.4300        | 3       |               |         |
| 2.2400        | 33      | 1.4000        | 3       |               |         |
| 2.1100        | 3       | 1.3600        | 1       |               |         |
| 2.0600        | 3       | 1.3400        | 3       |               |         |
| 2.0000        | 1       | 1.3000        | 7       |               |         |
| 1.9500        | 23      | 1.2700        | 3       |               |         |

tetrahedra. There are rings of ten tetrahedra joined up to form 3-dimensional networks. Now during vaporization or reaction with water the networks must be broken which needs extra energy.

TABLE 3.—X-RAY POWDER DIFFRACTION DATA FOR  $P_2O_5$  (T-FORM).

| $d\text{\AA}$ | $I/I_1$ |
|---------------|---------|
| 5.6800        | 80      |
| 4.6600        | 80      |
| 3.8800        | 80      |
| 3.6950        | 50      |
| 3.5850        | 50      |
| 3.3500        | 60      |
| 3.0300        | 100     |
| 2.7650        | 80      |
| 2.4340        | 60      |
| 2.3260        | 20      |
| 2.2380        | 20      |
| 2.1460        | 20      |
| 2.0650        | 10      |
| 1.9960        | 40      |

Fig. 1.—(a) IR spectrum of  $P_2O_5$  (O'-form). (b) IR spectrum of  $P_2O_5$  (H-form).

This is why the stable orthorhombic form of  $P_2O_5$  is less volatile and less hygroscopic. So this form of  $P_2O_5$  is suitable for using as a reagent.

**Acknowledgement.**—The author wishes to thank Dr. F. Sandford, Associate Professor, Silicate Research Institute, Chalmers University of Technology, Gothenburg, Sweden, for his constant interest in the progress of the work, the Swedish International Development Authority (SIDA) for granting me a fellowship for postgraduate studies in Sweden.

### References

1. W.L. Hill, G.T. Faust and S.B. Hendricks, *J. Am. Chem. Soc.*, **65**, 794 (1943).
2. A.F. Wells, *Structural Inorganic Chemistry*, 3rd edition (Oxford University Press, 1962), p. 646.
3. ASTM Index Card No. 1-0213.