X-RAY CRYSTALLOGRAPHIC STUDY OF THE CHANGE OF ORTHO-BORIC ACID DURING THERMAL TREATMENTS

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INTRODUCTION

In past years, Kracek, Morey and Merwin (1938), Cole and Taylor (1935) and McCulloch (1937) studied the different aspects of physico-chemical properties of oxyacids of boron. Recently Zachariasen (1954) has found the crystal structure of orthoboric acid, which is triclinic, with $a = 7{\cdot}039$Å, $b = 7{\cdot}053$Å, $C = 6{\cdot}578$Å and $\alpha = 92{\cdot}58°$, $\beta = 101{\cdot}17°$, and $\gamma = 119{\cdot}83°$. On thermal dehydration of orthoboric acid, the other important oxyacid of boron, i.e. metaboric acid, is formed in the temperature zone of 100°C.–125°C. The possible dehydration of orthoboric acid may be described in the following way.

$$4\ H_3BO_3 \rightarrow 4\ H_2O + 4\ HBO_2$$
$$4\ H_3BO_3 \rightarrow 5\ H_2O + H_2B_4O_7$$
$$4\ H_3BO_3 \rightarrow 6\ H_2O + 2\ B_2O_3$$

But unlike HBO_2 and B_2O_3, the existence of $H_2B_4O_7$ is very doubtful. Moreover, the condition of formation of metaboric acid HBO_2 and boric anhydride B_2O_3 depends on the temperature and the duration of heat treatment. Again metaboric acid is said to exist in three monotropic forms to each other. But so far no detailed X-ray study has been carried out on the dehydrated products of orthoboric acid. In the present paper, further informations of the structural details of the dehydrated products of orthoboric acid from X-ray study along with the thermal analysis have been given. Prior to X-ray study a preliminary thermal and differential thermal curves of orthoboric acid have been made so as to obtain valuable information over the temperature ranges, where structural changes occur. The experimental procedure was the same as that used by us (1955) in the case of anhydrous sodium sulphate and borax.

EXPERIMENTAL

Thermal Analysis.—It is expected that the complete analysis of thermal curve of orthoboric acid will reveal some interesting information concerning the phase-transformation of orthoboric acid. The thermal curves, both percentages of weight lost along with temperature and the differential thermal curve, have been shown in Figs. 1 and 2. Both the curves have been obtained in the usual standard process. In the former case a known amount of boric acid of 200 mesh grain size contained in a chemical resistant pyrex tube was placed for 20 hours in an electric oven and at each temperature at the interval of 10°C. the weight lost of the product was obtained. Thus a thermal curve is obtained by heating the specimens for equal periods at a series of temperatures. The ensuing curve of thermal analysis gives a distinct indication of some structural changes accompanying the different thermal treatments. It is

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evident that up to about 100°C. the loss in weight is small, then from 100°C. the loss in weight increases rapidly up to 140°C. and after that temperature again the loss in weight is small. The differential thermal curve shows only one endothermic peak. The physical characteristics of the substance also changes along with the temperature treatment. As a matter of fact, above 140°C. under the above experimental condition, the whole of boric acid transforms completely into a vitreous phase. In the present section, the X-ray studies were made of different samples of boric acid, heat-treated up to different temperatures where the structural changes occur. A number of dehydrated products of orthoboric acid of different thermal history were prepared and chemical composition of each specimen was determined. In that connection the B_2O_3 content of the specimen was determined by hydrating the known weight of the specimen to H_3BO_3 and then titrating boric acid solution by alkali in the usual process.

It is well known that metaboric acid HBO_2 forms in the range of temperature of 100°C. to 140°C. by the dehydration process, the higher the temperature the less is the time required for the complete conversion of orthoboric acid to metaboric acid. At first along with the metaboric acid there is some quantity of unconverted orthoboric acid, but after 125°C. there is practically no orthoboric acid provided the sample is kept at that temperature for 15 to 20 hours. Theoretically, it is known that 100 gms. of H_3BO_3 will yield 56·45 gms. of B_2O_3 or 70·89 gms. of HBO_2 after conversion to the respective compounds. The chemical analysis of the products proves unambiguously that the substance formed is pure metaboric acid. Again, the product formed at a temperature above 140°C. has a composition in between metaboric and boric anhydride, the higher the temperature of dehydration, its composition shifts more towards the B_2O_3. The X-ray diffraction study of the dehydrated products has been made so that the constituents present in different products may be identified. The X-ray photographs were taken in a cylindrical camera using CuKα radiation from a Hadding tube run at a voltage of 60 kV with a tube current of 10 mA and the specimen was taken in a very thin-walled dry glass capillary tube, which was later on sealed at both ends.

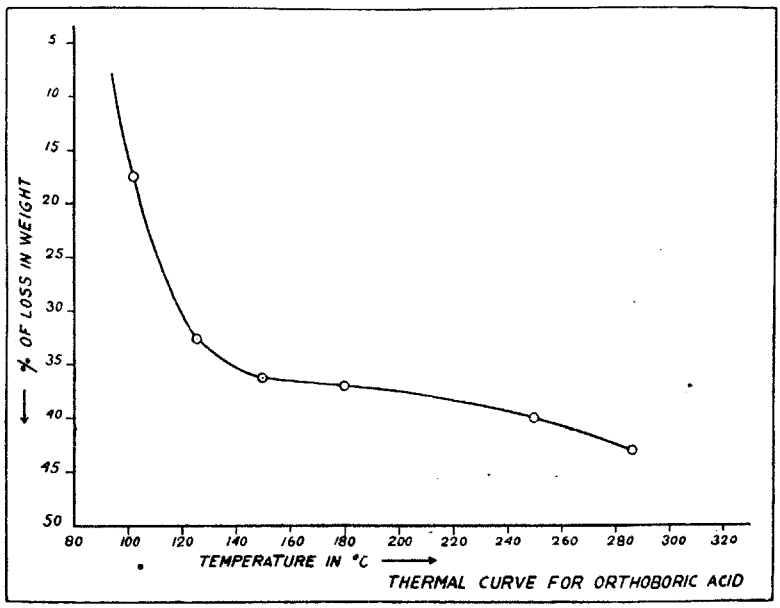

FIG. 1.

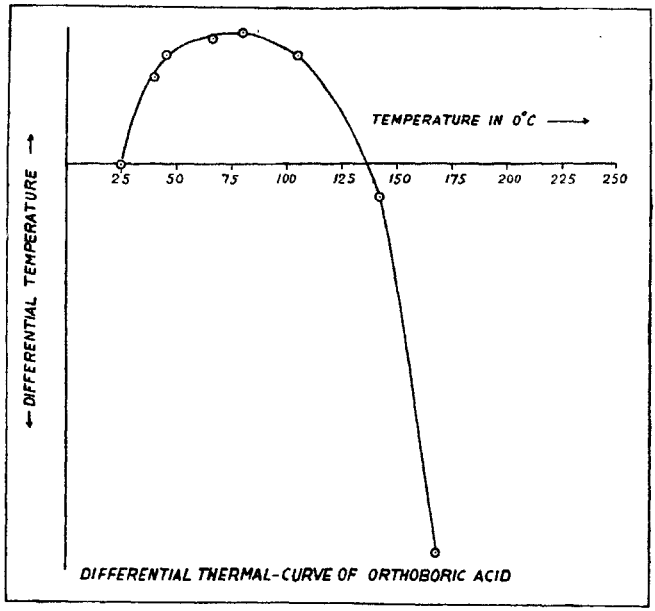

FIG. 2.

X-ray Analysis.—It is quite evident from Fig. 3 that the X-ray picture of each specimen depends on its thermal history. Metaboric acid obtained by the dehydration gives rise to X-ray diffraction pattern which is distinct from that of orthoboric acid. Again, the X-ray pattern of the dehydrated product obtained from 140°C. upwards is quite different from that of metaboric acid. In the former case, practically diffuse bands with a few lines are obtained in the X-ray picture while in the latter a number of lines are found in the X-ray picture. It is also observed that the specimens prepared at 145°C. for 15 hours give only diffuse bands. Density of that specimen determined by floatation method comes to about 1·827 in contrast with the value 1·8400 for pure B_2O_3 glass at 35°C. But in the case of other specimens prepared at a still higher temperature having the same period of heating, besides the above bands, some lines appear in the picture. The spacings of bands can be satisfactorily compared with those of pure B_2O_3 glass 4·1 A (S), and 2·1 A (W) and again some lines which are present along with bands in some specimens compare nicely with those of metaboric acid. In the case of metaboric acid, an attempt has been made to determine its crystal structure from its X-ray powder pattern. In that connection the spacing of each line has been accurately determined by taking the X-ray photograph of the specimen in a cylindrical camera.

CRYSTAL STRUCTURE ANALYSIS OF METABORIC ACID

The usual single crystal X-ray study by rotation and Weissenberg method would have been very useful in this case, but due to the fact that no good single crystal of appreciable size of metaboric acid can be found as well as due to its higher sensitivity towards moisture, the above method cannot be satisfactorily applied in the present case. Consequently, the present investigation was started from the powder pattern of metaboric acid.

Application of Hesse-method in the case of metaboric acid

As it has been already stated that no single crystal of appreciable size of metaboric acid was found, the method suggested by Hesse (1948), which was further modified by Stosick (1949), was applied in the determination of the crystal class of metaboric acid. This method of analysis was found to be useful by Dasgupta (1953, 1954) when all the other graphical and analytical methods gave rise to too much of difficulty.

The spacing of each line of metaboric acid is transformed into $\sin^2\theta$. Complete data of each line along with the relative intensity are given in Table I. The crystal class and the space-group of metaboric acid have been determined in the following way.

Table I

X-ray data of metaboric acid

	Intensity	sin θ	d in Å	$\sin^2\theta$
7° 27′	s	0·1297	5·933	0·0168
8° 41′	w	0·1509	5·100	0·0228
10° 6′	m.w.	0·1754	4·388	0·0305
10° 49′	w	0·1876	4·103	0·0352
12° 46′	m.s.	0·2299	3·485	0·0488
14° 17′	v.s.	0·2468	3·119	0·0609
15° 32′	w	0·2679	2·873	0·0718
18° 7′	m	0·3109	2·476	0·0967
19° 21′	m	0·3313	2·324	0·1098
20° 26′	m	0·3491	2·206	0·1218
21° 57′	v.w.	0·3738	2·060	0·1398
23° 0′	m	0·3906	1·970	0·1526
24° 31′	n.w.	0·4149	1·956	0·1718
25° 25′	v.v.w.	0·4292	1·793	0·1842
27° 5′	m	0·4550	1·692	0·2070
29° 35′	w	0·4936	1·560	0·2437
35° 5′	v.v.w.	0·5748	1·340	0·3298
41° 38′	m.w.	0·6643	1·159	0·4414

Determination of the Crystal Class

The following are the q or $\sin^2\theta$ values observed for the first 10 lines of the diffraction pattern of HBO_2 corrected up to fourth places:—

$q_1 = 0{\cdot}0168$ $\quad$ $q_6 = 0{\cdot}0609$
$q_2 = 0{\cdot}0278$ $\quad$ $q_7 = 0{\cdot}0718$
$q_3 = 0{\cdot}0305$ $\quad$ $q_8 = 0{\cdot}0967$
$q_4 = 0{\cdot}0352$ $\quad$ $q_9 = 0{\cdot}1098$
$q_5 = 0{\cdot}0488$ $\quad$ $q_{10} = 0{\cdot}1218$

It is seen from the above that

(1) $8q_3 = 5q_5$
(2) $q_6 = 2q_3$
(3) $2q_6 = q_{10}$
(4) $4q_6 = 5q_5$
(5) $q_{10} = 4q_3$

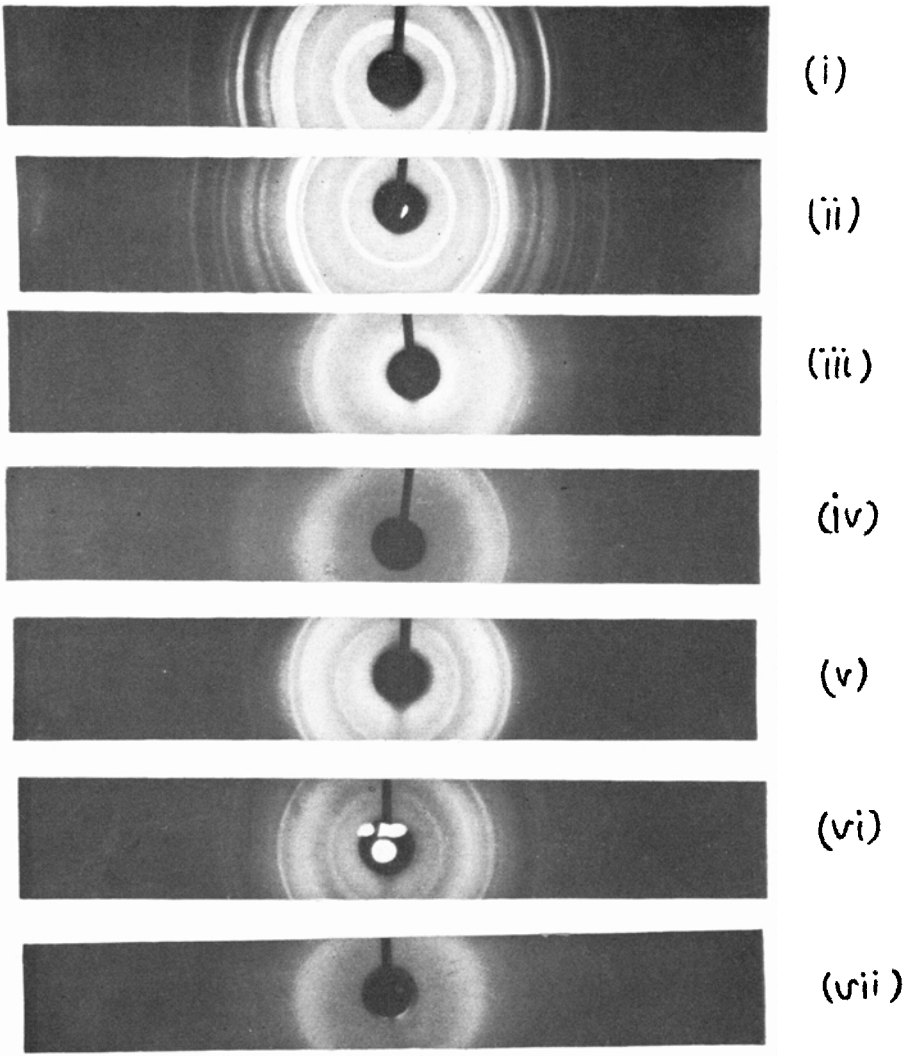

FIG. 3. X-ray diffraction patterns of orthoboric acid.

(i) At room temperature, (ii) heated to 125°C., (iii) heated to 145°C., (iv) heated to 200°C., (v) heated to 227°C., (vi) heated to 290°C., (vii) pure B_2O_3 glass.

The above relations are of the type $m_1q_1 = m_2q_2$. So the crystal class must be either cubic or tetragonal or hexagonal. That HBO_2 does not possess a cubic symmetry is definite from the pattern itself. So it must be either tetragonal or hexagonal. The sequences of the M values in the observed relations are 1, 2, 4, 5, 8, which show that HBO_2 must belong to the tetragonal class.

Now, from the relation $8q_3 = 5q_5$ it is likely that M_3 (l_3 in this case being zero), should be equal to 5 or to its multiples. If we now take $M_3 = 5$, then $A_3 = 0{\cdot}00609$ (from the relation $q = AM+CN$, N being zero in this case). With this value of A_3 as A, we find that when $M_1 = 1$,

$$Cl_1^2 = q_1 - AM_1 = 0{\cdot}01683 - 0{\cdot}00609 = 0\,01074 = q_{8/9}.$$

If we now take the M values for q_8 to be zero, then we get $Cl_1^2 = Cl_{8/9}^2$ from the equations $Cl_1^2 = q_{8/9}$ and $q_8 = Cl_8^2$. Wherein if we put $l_1 = 1$, $l_8 = 3$, then C comes out as 0·01074. All the lines can now be indexed with the help of the equation ($q = AM+Cl^2$), taking A 0·00609 and C 0·01074. The axial lengths, as calculated by $\left(A = \frac{\lambda^2}{4a^2}\right)$ and $\left(C = \frac{\lambda^2}{4c^2}\right)$, are $a = b = 9{\cdot}865$ Å, $C = 7{\cdot}427$ Å. Table II gives the $\sin^2\theta$ values (calculated and observed) and the $h\ k\ l$ values of all the lines observed in the pattern.

TABLE II

Comparison of the Calculated and Observed $\sin^2\theta$ Values and the $h\ k\ l$ Values for the Powder Lines

$\sin^2\theta$/obs	$h^2+k^2(M)$	l^2 (N)	$h\ k\ l$	$\sin^2\theta$/cal.
0·0168	1	1	101	0·0168
0·0228	2	1	111	0·0229
0·0305	5	0	210	0·0305
0·0352	4	1	201	0·0351
0·0488	8	0	220	0·0487
0·0609	10	0	132	0·0609
0·0718	10	1	131	0·0716
0·0967	0	9	003	0·0966
0·1098	18	0	330	0·1098
0·1218	20	0	240	0·1218
0·1398	16	4	402	0·1398
0·1526	25	0	500 or 340	0·1523
0·1718	0	16	004	0·1718
0·1842	2	16	114	0·1840
0·2070	34	0	350	0·2070
0·2437	40	0	620	0·2436
0·3298	26	16	154	0·3298
0·4414	9	36	306	0·4414

DETERMINATION OF THE SPACE-GROUP

The axial lengths and the indices for all the powder lines now being determined, the space-group can be found out. The density of HBO_2, determined with the help of a pyknometer in the well-known floatation method, was 1·60 gm./cm^3. The axial parameters and the density then allow only 16 molecules in the unit cell. From Table II it can be seen that there are no systematic absences in any order of reflecting planes, whence it can be concluded that the most suitable space-group for HBO_2 is $D_4^1\ h$ or $P\ 4/m\ m\ m$.

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Abstract

The complete phase-transformation of orthoboric acid during thermal treatment has been studied by thermal, differential thermal and X-ray method of analysis. Along with that the crystal class to which metaboric acid belongs has been found out directly from the powder pattern of metaboric acid.

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