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Infrared Spectroscopic Studies of Boron Phosphate and Adsorbed Species

I. Effects of Evacuation at Elevated Temperatures and the Adsorption of Water

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The effect of heating and evacuation, and the adsorption of water on boron phosphate (BPO_4) has been investigated by infrared spectroscopy. Three high surface area BPO_4 samples, with phosphoric to boric acid ratios of 0.8, 1.0, and 1.2 and a low surface area sample were employed. The spectra indicated that water adsorbed on dehydrated BPO_4 was partially dissociated. Bands assignable to BOH and POH were found, and confirmed from shifts on deuteration. Formation of HO—P=O can be correlated with the disappearance of non-hydrogen-bonded P=O. A "strained" or bridged oxide site, which may be responsible for the catalytic activity of BPO_4 in dehydration reactions, is postulated to explain the dissociation of water.

INTRODUCTION

Boron phosphate, in its common form, is a white microcrystalline solid, which may be considered as a mixture of the anhydrides B_2O_3 and P_2O_5 (*1*). Although BPO_4 occurs in several crystallographic forms, isostructural with one or more forms of silica, the low density modification of BPO_4 is the most common and has a structure similar to cristobolite. A tetrahedral bipyramidal structure, consisting of alternate B^{3+} and P^{5+} atoms, both tetrahedrally coordinated to oxygen, has been proposed (*1, 2*), and this has been, in part, substantiated through nuclear magnetic resonance and infrared spectroscopic studies (*3–6*).

Previous work on the surface and catalytic properties of BPO_4 in this and other laboratories has been summarized earlier (*7*). Since that time studies of the adsorption of krypton and of argon over wide ranges of temperature and pressure have been completed (*8*). These show that, among other things, the surface of BPO_4 is quite heterogeneous but somewhat surprisingly, the effect of evacuation with heating at different temperatures alters the heterogeneity, as evidenced from the calculated isosteric heats of adsorption, relatively little. Scanning electron microscopy (*9*) performed on BPO_4 with various amounts of adsorbed water have shown that although small changes in the surface can be observed with small amounts of water adsorbed, massive structural changes do not occur until the relative pressure of water vapor is quite high.

Earlier work in this laboratory employing electron spin resonance (*10*) and diffuse reflectance (*11*) spectroscopy in the study of some adsorbed organic compounds suggested a similarity between BPO_4 and silica–alumina and demonstrated the presence of both Lewis and Bronsted acid sites, with the former apparently predominating. However some recent work (*12*) in our laboratory on the decomposition of ethanol vapor over BPO_4 tends to favor a similarity between BPO_4 and alumina.

It became obvious some years ago that more information about the types of surface species was needed, and for this reason an infrared spectroscopic study was initiated. In spite of the abundance of such data for some catalysts, relatively little spectroscopic work has been reported on BPO_4.

As has been mentioned, Dachille and Roy (*5*) and Weir and Schroeder (*6*) were the first to apply infrared spectroscopy to boron phosphate and did so in order to determine the coordination number of boron in BPO_4. Gesmundo and Lorenzelli (*13*) carried out a detailed infrared spectroscopic investigation of the solid and were able to assign many of the vibrational modes. Kubasov and Kitaev (*14*) have recently reported the results of a potassium bromide matrix ir study of the bulk structure of BPO_4. It thus appears that there have been no infrared studies prior to the present one on the surface species associated with BPO_4. However, there have been several such studies reported on other phosphates and oxides of boron and phosphorus. These will be cited later during the discussion of band assignments.

As has been mentioned, information obtained (*10–12*) in this laboratory suggests that BPO_4 contains on its surface both Bronsted and Lewis acid sites and in addition, that the catalytic activity is, at least in part, related to the presence of such sites. Hence it appeared desirable to begin our infrared spectroscopic studies by determining what types of groups exist on the surface of BPO_4 and the effect of evacuation with heating on such groups.

Experimental Methods

BPO_4 of both high surface area 50–200 $m^2\,g^{-1}$) and low surface area (less than 50 $m^2\,g^{-1}$) was employed in this work. The preparation of both types of samples is described in detail elsewhere (*12, 15*). The high area samples were made from tri-*n*-propyl borate (*15*) and 85.6% ortho phosphoric acid (*12*), while the low area samples were obtained from the reaction of the latter acid with boric acid (*12*). Some of the samples were treated in an infrasizer air elutriator (Infrasizer Ltd. Toronto) to yield a product with average particle size less than 5 μm as estimated from scanning electron microscope photographs. All samples were stored, under vacuum, in sealed glass vials.

Self-supported pellets of BPO_4 were prepared by pressing 80–90 mg of boron phosphate between two Teflon plates (1.8 × 2.9 cm and 1/16 in. thick) which were sandwiched between two pieces of stainless steel, at a pressure of 8000–10,000 lb/in.^{2}. This pressure resulted in only approximately 2% decrease in surface area.

The infrared vacuum cell was similar to the type used by Peri and Hannan (*16*) with modifications to permit mounting in a vertical position in the Beckman IR-9 spectrometer. The Vycor cell was equipped with a small furnace built around its upper portion and calcium fluoride windows (Barnes Engineering) sealed with Torrseal epoxy resin (Varian Associates) which were air cooled. In addition, an evacuable reference cell with the same path length as the experimental cell, was built to fit into a standard liquid cell holder. The temperature of the furnace used with the experimental cell was monitored with a calibrated Chromel–Alumel thermocouple which was also employed to obtain a temperature profile for the furnace. The temperature was controlled to ±2°C.

After the freshly pressed pellet had been placed in the cell, pumping was begun and continued for up to 5 hr after which the furnace temperature was increased to 150°C over a period of 1 hr. If a higher initial pretreatment temperature was desired, the furnace temperature was raised from 150°C to the desired temperature over a period of 1 hr. This procedure was followed for all freshly pressed pellets in order to minimize the possibility of cracking.

Standard vacuum equipment and procedures were used throughout the work.

Results

Although the present interest was primarily in the portion of the spectrum of boron phosphate resulting from surface species, nevertheless bands due to bulk vibrations had to be identified and distinguished from those due to surface species.

TABLE 1

BORON PHOSPHATE STRUCTURAL COMBINATION AND OVERTONE BANDS (4000–1300 cm^{-1})

Sample	Infrared absorption bands
BP(TB-9,10α) evacuated 500°C	2315 m, 2150 s, 1836 s, 1733 w, ca. 1660 m
BP(TB-9,10α) evacuated 700°C	2580 w; 2418 w; 2325 m; 2310 w, sder; ca. 2250 w, sder; 2152 s, 1935 m; 1840 s; ca. 1770 wb; 1732[a] m; 1645[a] m; 1530[a] w; ca. 1390[a] m?
BP(TB-11) evacuated 700°C	ca. 2580 w; 2418 w; 2326 m; 2310 w, sder; 2265 wb; 2153 s, ca. 2060 wb?, 1938 m, 1831 s, ca. 1770 wb; 1735 m; ca. 1665 w, sder; 1650 m; 1534 m; ca. 1385 m
BP(TB-12) evacuated 700°C	ca. 2420 w; 2320 m; ca. 2250 wb; 2155 s; 1938 m; 1842 s; ca. 1780 wb; 1738 m; 1650 mb; ca. 1440[b] vsb
BP(RS-2,3α) evacuated 100°C	2418 w; 2322 msh; 2308 w, sder; 2248 wb; 2151 s; ca. 2060 wb; 1934 s; 1895 m; 1837 sb; 1772 w, sder; 1732 s; 1668 w, sder; 1648 s; 1623 w, sder; ca. 1560 w, sder; 1536 s; 1485 w; 1438 w; 1390 m

[a] These bands may be due to surface species.

[b] This band may be due to bulk $B(OH)_3$.

TABLE 2

INITIAL SURFACE AREAS AND PHOSPHORUS/BORON RATIOS OF SAMPLES OF BORON PHOSPHATE

Sample no.	P_2O_5/B_2O_3 (M)	Surface area (m^2/g)
TB-9,10α	1.00	118
TB-11	1.2	69
TB-12	0.8	138
RS-2,3α	1.15	20

Table 1 lists those bands believed to be combination and overtones for four different boron phosphate samples, identified in Table 2. It was found necessary to restrict investigations to the 4000–1300 cm^{-1} region since fundamental lattice vibrations almost completely obscured the 1300–400 cm^{-1} region. As can be seen from the figures the BPO_4 samples became more transparent when evacuated at progressively higher temperatures. Most BPO_4 samples had to be heated over 300°C before bands in the 1800–1300 cm^{-1} range could be resolved with any degree of accuracy.

The changes produced in the infrared spectrum of samples of boron phosphate as a result of heating while pumping are illustrated in Figs. 1–4. Table 3 provides data on the change in surface area and weight on heating of two of the samples. As can be seen BPO_4 pellets prepared and

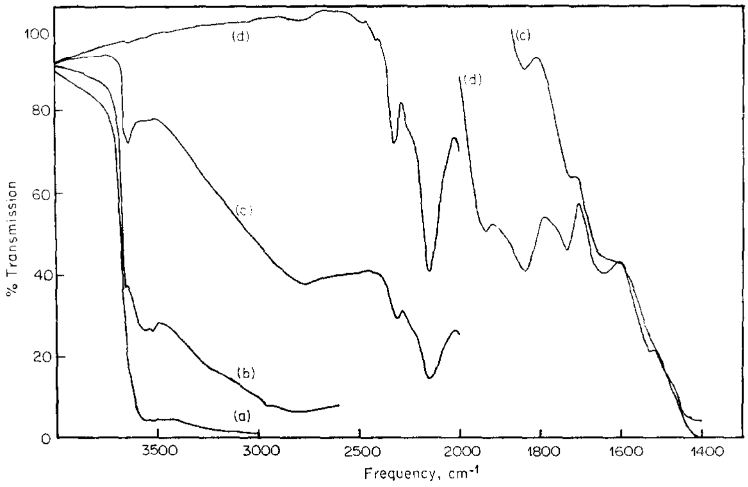


FIG. 1. Infrared spectra of BP(TB-9,10α)-4 evacuated at progressively increasing temperatures. Evacuated: (a) 150°C, 18.5 hr; (b) 300°C, 19 hr; (c) 500°C, 15 hr; (d) 700°C, 14.5 hr.

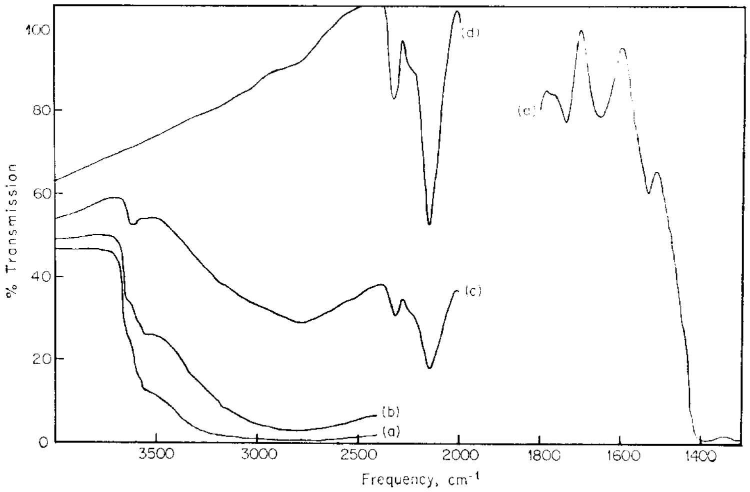


FIG. 2. Infrared spectra of BP(TB-11)-1 evacuated at progressively increasing temperatures. Evacuated: (a) 150°C, 8 hr; (b) 300°C, 8 hr; (c) 500°C, 8 hr; (d) 700°C, 8 hr.

evacuated at room temperature were relatively transparent to infrared only above 3500 cm^{-1}, while below 3500 cm^{-1}, percentage transmission was generally less than 1%. Fluorolube mull spectra evacuated at room temperature showed that the low transmission below 3800 cm^{-1} was due to strong absorption bands at 3380 and 1635 cm^{-1}, overlapping with a band near 2800–2900 cm^{-1}. These bands are probably due to sorbed water and *n*-propanol. Table 4 summarizes the band assignments for the various surface hydroxyl groups. Justifications for such assignments are discussed below.

Figure 1 shows the spectroscopic changes for sample TB-9,10α which was a high area sample of P/B ratio equal to 1. When evacuated at 150°C (Fig. 1), a strong broad band was noted at 2810 (I), overlapping with a band near 3320 (II). A weak band appeared as a shoulder at 3670 (III);

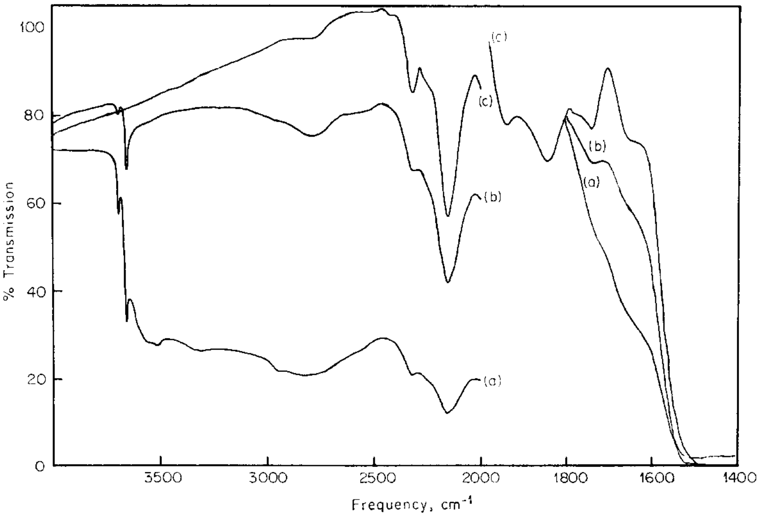


FIG. 3. Infrared spectra of BP(TB-12) evacuated at progressively increasing temperatures. Evacuated: (a) 300°C, 8 hr; (b) 500°C, 8 hr; (c) 700°C, 5 hr.

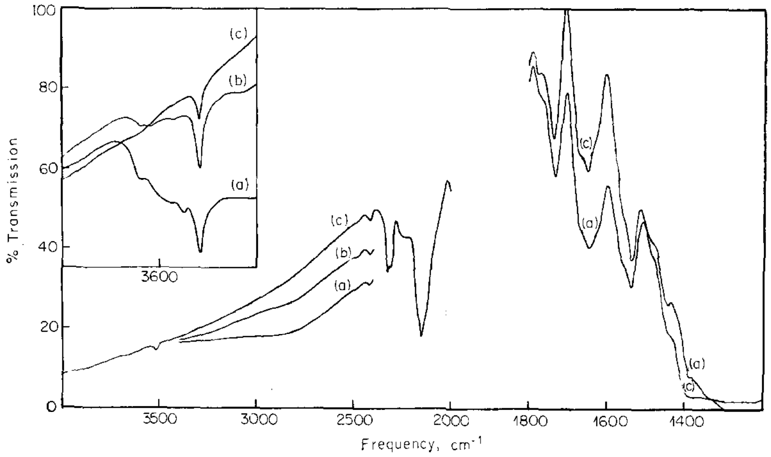


FIG. 4. Infrared spectra of BP(RS-2,3α)-2 evacuated at progressively increasing temperatures. Evacuated: (a) 300°C, 4 hr; (b) 500°C, 8 hr; (c) 700°C, 10 hr.

medium bands at 3590 (IV) and 3550 (V). Also, a weak band appeared at 3520 (VI) on evacuation at 300°C; band I and II decreased and shifted to 2780 and 3300 cm^{-1}; III shifted to 3656 cm^{-1}, IV decreased greatly, and V possibly decreased and shifted to 3555 cm^{-1}. A weak band appeared at 3635 cm^{-1} (VII). On evacuation at 500°C, band I decreased and shifted to 2770; 3300 disappeared, III decreased and became a shoulder at 3654, while VII at 3634 cm^{-1} increased. IV, V, and VI appeared as a weak broad tail, from 3600 to 3500 cm^{-1}. On evacuation at 700°C, these bands were almost completely removed. Band I shifted to 2760 cm^{-1}, and VII was still present as a weak band. Evacuation at 800°C appeared to remove all of these bands completely.

TABLE 3
WEIGHT LOSS AND CHANGE IN SURFACE AREA ON HEATING

Preheat temp (°C)	Surface area (m^2/g)	%Wt of sample evacuated at room temp
Boron phosphate BP(TB-9,10α)[a]		
25.5	118.2	100.0
315	135.3	95.0
488	134.5	93.3
687	101.2	92.1
Boron phosphate BP(RS-2,3α)		
23	18.6	100.0
326	37.8	92.8
504	38.7	91.5

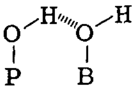
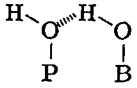
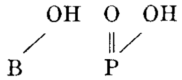
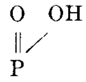
[a] Pressed pellet sample. Surface area of unpressed BP(TB-9,10α) was 121.1 m^2/g.

A comparison of the spectra obtained on other samples of BPO$_4$ after heating and evacuation is of interest. Figure 2 shows the spectra for TB-11, a relatively high surface area sample with a P/B ratio of 1.2, that is, an "excess" of phosphorus. The spectra for this sample are basically similar to those for TB-9,10α (Fig. 1), although the 3560 cm^{-1} band (V) may be larger for TB-11.

The spectra (Fig. 3) of TB-12 (a high boron BPO$_4$) are substantially different from that for TB-9,10α and TB-11. Sharp peaks appeared at 3696 (VIII) and 3664 (III) on 300°C evacuation of the high boron sample. Also, bands at 3595 (IV) and 3310 (II) were larger, and the 2800 cm^{-1} band (I) smaller than for similar bands found for TB-9,10α evacuated at 300°C. When TB-12 was evacuated at 500°C, band VIII was reduced, while band III was both reduced and shifted to 3660 cm^{-1}. The 3640 cm^{-1} band (VII) noted for TB-9,10α did not appear for TB-12. Evacuation of TB-12 at 700°C completely removed bands III and VIII. A weak band was still present at 2800 cm^{-1}.

TABLE 4

BORON PHOSPHATE: BAND ASSIGNMENT FOR SURFACE HYDROXYL GROUPS

Band no.	Frequency (cm^{-1})	Assignment	Refs.
VIII	3700–3696	"Free" or unperturbed B–OH	(*33*, *34*, *18*)
III	3670–3654	"Free" P–OH	(*19*, *21*, *20*)
VII	3640–3630	Geminal POH	(*22*)
IV	3595	Associated with B H-bonded adjacent OH? 	
V	3554	Associated with P H-bonded adjacent OH 	
IX	ca. 3400; 1640	Sorbed H_2O (molecular)	(*17*)
VI	3518–3522 (1645? 1532?)	Interstitial OH or H_2O	(*25*)
II	ca. 3300	 Associated with B? or H_2O-bonded to surface O's.	(*23*)
I	2830–2790	 and H_2O H-bonded on surface O's?	(*19*)

The spectra and changes on heating for sample RS-2,3α (Fig. 4), a low surface area BPO_4 made from boric acid and orthophosphoric acid, appeared similar to that for TB-9,10α. However, the band at 3518 cm^{-1} (VI), only observed as a weak band for high surface area BPO_4, was very prominent for RS-2,3α. This band was reduced but not removed by evacuation at 700°C.

The readsorption of water at various temperatures was investigated spectroscopically for BPO_4 samples evacuated at 300, 500, and 700°C. For TB-9,10α evacuated at 700°C, and water adsorbed at 30°C (Figs. 5A–C), a peak appeared initially at 3600 cm^{-1} (IV) with a smaller peak at 3692 (VIII), and a broad strong band near 2830 cm^{-1} (I). As discussed below, bands IV and VIII probably represent OH groups and that at 2830 cm^{-1} either water H-bonded on surface oxygen atoms or possibly groups in which an oxygen is double-bonded to a P atom to which an OH group is also attached.

As more water was adsorbed, IV and VIII decreased and shifted upward to 3668 (III) and 3696 (VIII) cm^{-1}, respectively, while band I increased and shifted to 2860 cm^{-1}. On high coverage with water, a broad band (IX) appeared near 3500–3300 cm^{-1}. This band IX appeared to be removed almost entirely on evacuation at 30°C [Fig. 5B(e)], and hence may represent either a form of hydrogen-bonded BOH or strongly adsorbed molecular water.

On evacuation at 150°C, band VIII (3696 cm^{-1}) appeared to disappear but band

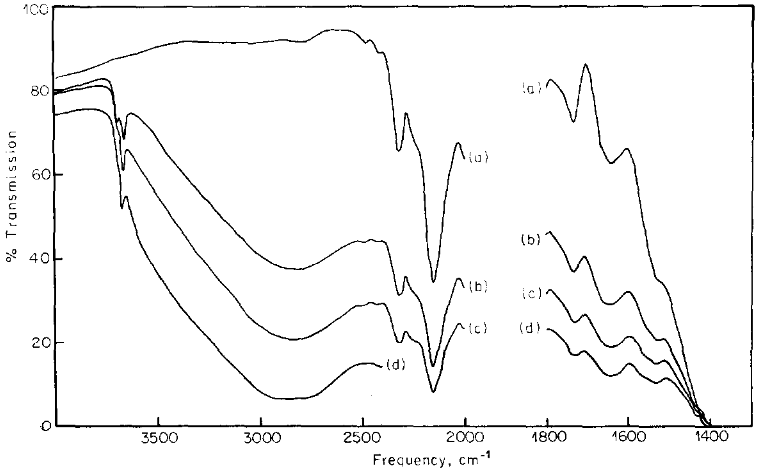


FIG. 5A. Infrared spectra of BP(TB-9,10α)-8 evacuated at 700°C; water adsorbed at 30°C. (a) Evacuated 150°C, 24 hr; 700°C, 18 hr; (b) exposed to water vapor, 0.2 Torr, 30°C, 2 min; (c) exposed to water vapor, 2.6 Torr, 30°C, 1 hr; (d) exposed to water vapor, 6.4 Torr, 30°C, 12 hr (all samples evacuated 10 min, 30°C prior to determining spectrum).

III increased, reached a maximum at 300°C, decreased on evacuation at 500°C, and shifted from 3664 cm^{-1} at 30°C to 3648 at 600°C. At 300°C a tail appeared on band III, resolving into a band at 3636 cm^{-1} on 450°C evacuation, and decreased at 600°C evacuation.

Band I decreased steadily with evacuation, shifting downward from near 2840 cm^{-1} at 30°C to 2780 cm^{-1} at 600°C.

The bands in the OH bending region showed an increase for 1640, 1532, and possibly 1440 cm^{-1} on adsorption of water, and decreased on desorption.

The adsorption of water on BP(TB-9,10α) evacuated at 500°C (Fig. 6) appeared to be similar to 700°C evacuation. On water adsorption, the band at 3634 disappeared and did not reappear until the water was desorbed at 300°C. On desorption, an additional band, which may not appear for water adsorption on BP(TB-

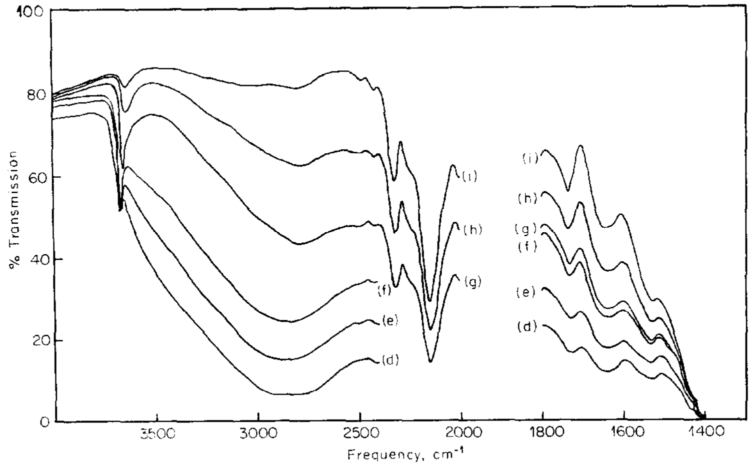


FIG. 5B. Infrared spectra of BP(TB-9,10α)-8 evacuated at 700°C; water adsorbed at 30°C; desorbed at progressively increasing temperatures. (e) Evacuated 700°C, exposed to water vapor, 30°C; evacuated 30°C, 16.5 hr; evacuated: (f) 150°C, 8 hr; (g) 300°C, 8 hr; (h) 450°C, 4 hr; (i) 600°C, 4 hr.

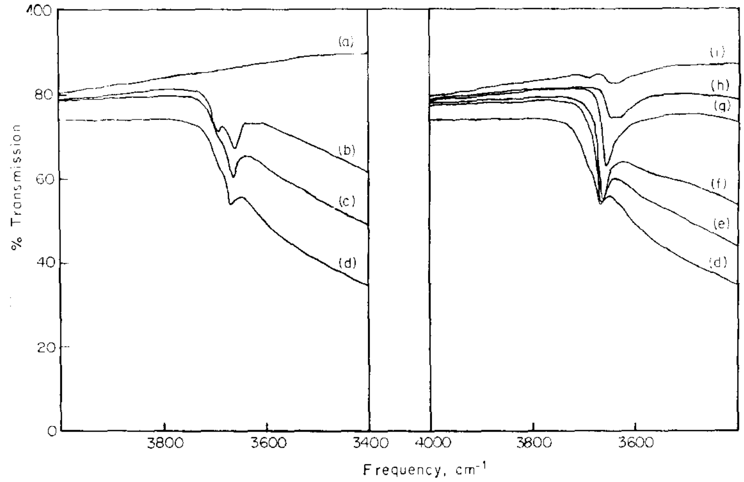


FIG. 5C. Infrared spectra of BP(TB-9,10α)-8; (a) evacuated at 700°C for 18 hr; (b) exposed to water vapor at 30°C: 2 min, 0.2 Torr; (c) 1 hr, 2.6 Torr; (d) 12 hr, 6.4 Torr; evacuated: (e) 30°C, 16.5 hr; (f) 150°C, 8 hr; (g) 300°C, 18 hr; (h) 450°C, 4 hr; (i) 600°C, 4 hr.

9,10α) preheated at 700°C, was noted at about 3300 cm^{-1}. Also, the bands near 3600 appeared stronger than in the case of the 700°C preheat. After the adsorption of water the sample which had previously been evacuated at 500°C was again subjected to the latter treatment. The resulting spectrum was similar to that obtained before water adsorption, suggesting a reversible adsorption of water.

For a high phosphorus BPO_4 preheated at 700°C, the results for water adsorption were essentially the same as those for (TB-9,10α). However, for high boron BPO_4 (Fig. 7), on water adsorption, peaks appeared at 3696 and 3666 cm^{-1} with the former being much larger than the latter. Strong broad bands were observed near 3420 and 3050 cm^{-1}, while the band at 1640 cm^{-1} increased.

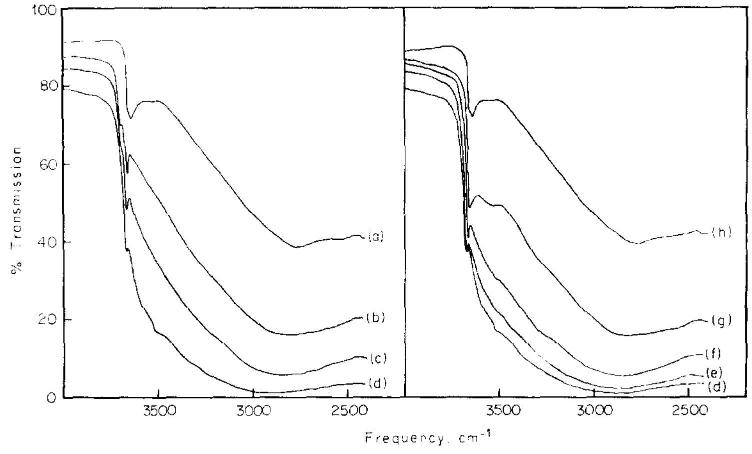


FIG. 6. Infrared spectra of BP(TB-9,10α)-10 evacuated at 500°C water adsorbed at 30°C; water desorbed at progressively increasing temperatures. (a) Evacuated 150°C, 24 hr; 500°C, 12 hr; (b) 1.0 Torr water vapor, 30°C, 5 min; (c) 2.1 Torr water vapor, 30°C, 1 hr; (d) 5.3 Torr water vapor, 30°C, 12 hr; (e) evacuated 30°C, 10 hr; (f) 150°C, 8 hr; (g) 300°C, 8 hr; (h) 500°C, 5 hr; (b, c and d) evacuated 10 min, 30°C prior to determining spectrum.

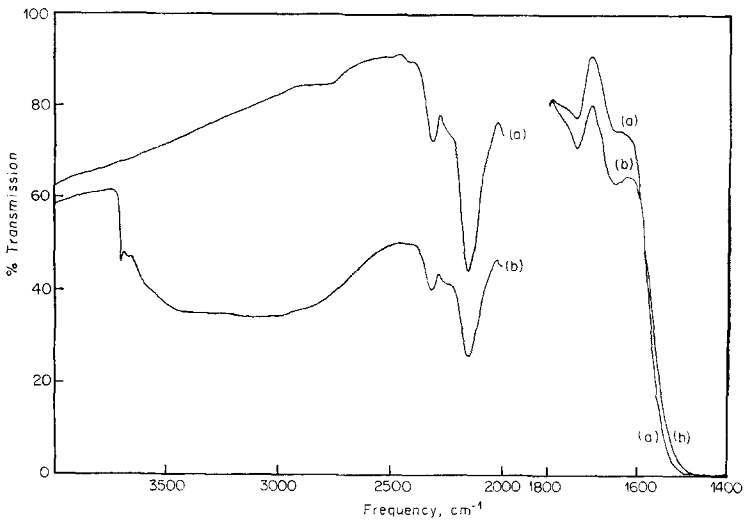


FIG. 7. Infrared spectra of BP(TB-12)-1 evacuated at 700°C water adsorbed at 30°C. (a) Evacuated 700°C, 5 hr; (b) 0.5 Torr water vapor, 30°C, 2 min; evacuated 30°C, 10 min.

Isotopic exchange experiments with D_2 and D_2O suggest that the bands at 3696, 3666 to 3652, approximately 3640 and 3520, 3590, and 3558 cm^{-1} are due to hydroxyl groups. The frequencies before and after deuteration and the corresponding ratios are listed in Table 5. The shift of the 3320 cm^{-1} band seems rather low even considering that the ratio for most surface OH groups is usually closer to 1.35 (*17*) rather than the theoretical value of 1.37.

TABLE 5
FREQUENCY RATIOS FOR BORON PHOSPHATE HYDROXYL AND DEUTEROXYL GROUPS

Sample	ir bands (cm^{-1})	$\bar{\nu}_{OH}/\bar{\nu}_{OD}$
BP(TB-9,10α) evac. 500°C,	3652; 2694	1.356
D_2 exchanged 300; 500°C	3644; 2677	1.361
BP(TB-9,10α) evac. 300°C;	3518; 2605	1.350
D_2O 30°C	3590; 2660	1.350
	3320; 2480	1.339
	3558; 2640	1.348
	3654; 2695	1.356
BP(TB-9,10α) evac. 700°C,	3694; 2727	1.355
D_2O 150°C	3664; 2702	1.356
BP(TB-9,10α) evac. 800°C; D_2O 30°C	3664; 2706	1.354
BP(TB-9,10α) evac. 500°C,	3656; 2699	1.355
D_2O 300°C	3590; 2650	1.355
	3518; 2606	1.349
BP(RS-2,3α) evac. 700°C, D_2O 30°C	3664; 2704	1.355

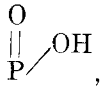
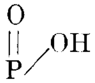
DISCUSSION

The results from the experiments involving the adsorption and desorption of water show that some forms of surface hydroxyls exist on boron phosphate. The bands were assigned by comparing relative ease of desorption, perturbing effects of water adsorption with differences between high B and high P BPO_4 and by comparison with the spectra of other oxides similar to boron phosphate. The presence of surface hydroxyls was also confirmed by deuterium and deuterium oxide exchange. Table 4 summarizes the assignments of bands which are discussed below.

The sharp peaks at 3700–3696 cm^{-1} and 3670–3654 cm^{-1} are attributed to some form of "free" or unperturbed OH, that is, B–OH and P–OH, respectively. These bands could represent isolated OH groups on the surface, or adjacent hydroxyl groups with one OH hydrogen bonded, leaving the other OH relatively unperturbed. This assignment is confirmed by comparison with the spectra for the high boron and high phosphorus BPO_4, since the 3696 cm^{-1} band is larger in the high boron BPO_4, and the 3670 band is larger in the high phosphorus sample. Also a band near 3700–3704 cm^{-1} has been noted by Cant and Little (*18*) for boron oxide supported on silica or porous glass, and this band has been assigned to free BOH. A band near 3663–3666 cm^{-1} has been noted for P_2O_5–SiO_2 by Low and Ramamurthy (*19*), one at 3680 for high surface area aluminum phosphate (*20*) and one at 3664 cm^{-1} for hydroxyapatite (*21*) assignable to free P–OH or geminal P–OH. Hair and Hertl (*22*) noted bands at 3700 and 3680 that were assigned to POH, the higher frequency possibly to a free OH, the lower frequency to a geminal OH. On this basis, the 3700 band appearing in boron phosphate could be assigned to POH. Hair and Hertl also found that both bands were perturbed equally by ammonia adsorption. However, with boron phosphate, on the addition of ammonia the 3664 band disappears completely while the 3696 band appears to be unaffected by the ammonia, suggesting that the two hydroxyl groups are essentially different. Thus, the assignment to B–OH for the 3696 band was preferred. Hair and Hertl also suggested that geminal P–OH is less readily desorbed than the isolated hydroxyl groups, and consequently the lower frequency band at 3634–3640 cm^{-1} that appears when BP(TB-9,10α) is evacuated above 300°C was assigned to geminal P–OH.

Comparison of BP(TB-9,10α), with both the high P and the high B samples indicates that in the latter the 3595 cm^{-1} is larger while in the former the 3555 cm^{-1} band is higher, suggesting that 3595 and 3555 cm^{-1} bands should be associated with B and P, respectively. The broadness of these bands suggests H-bonding interactions are involved, possibly from adjacent OH groups. The band near 3590 cm^{-1} appears to be perturbed only slightly by water adsorption while the 3555 cm^{-1} band is strongly influenced, which suggests that the latter is due to a surface species. The 3555 cm^{-1} band decreases on exposure of BPO_4 to water which suggests, since water adsorption is known to reduce the surface area of BPO_4 by closing up pores, that the 3555 cm^{-1} bands may be due to hydroxyl groups in the pores.

The band appearing near 3300 cm^{-1} on BPO_4 evacuated at 300°C is assigned to a form of hydrogen-bonded BOH, in part as a consequence of its increased intensity for high boron BPO_4. A band at 3230 cm^{-1} which appears with boric acid heated at 300°C could be due to strongly adsorbed molecular water, as found for alumina (*23*), assuming that chemisorbed molecular water is still present on the surface of BPO_4 after evacuation at 300°C.

The strong broad band appearing in the 2800–2770 cm^{-1} region can be reasonably assigned to  $\overset{\displaystyle O}{\overset{\|}{P}}\!\diagup OH$, as indicated by Bellamy (*24*). The low frequency of this band indicates a stronger hydrogen-bonding interaction than normal for hydroxyl groups, as in the case of phosphoric acid. Low (*19*) also assigned  $\overset{\displaystyle O}{\overset{\|}{P}}\!\diagup OH$ to a broad band at 2800 cm^{-1} for P_2O_5 on silica. The band near 2800 cm^{-1} shifts to higher frequencies on the adsorption of more water vapor. This shift may be due to overlap with bands due to molecular water at 3400 cm^{-1}, or alternatively to water which is hydrogen-bonded to surface oxygen or to P=O.

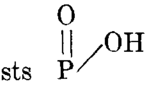
The band at 3522–3518 cm^{-1} shows only weakly for BP(TB-9,10α), but strongly for low surface area BP(RS-2,3α). This band is also present on other boron phosphate samples, notably samples from Victor and from Allied Chemicals. For BP(RS-2,3α) this band appears to be relatively unaffected by water adsorption at low temperatures, although for BP(TB-9,10α) there may be slight shifts. Although this band is weak for BP(TB-9,10α), exposure to water vapor at elevated temperatures causes an increase, small for 150°C but substantial for 300°C. This may explain why the band is stronger for BP(RS-2,3α) since this sample was prepared in an aqueous environment, and then calcined in air at 300°C. A sample of BP(TB-9,10α) calcined in air at 500°C also shows this band; the spectrum also appears similar to that of BP(RS-2,3α). The frequency of the 3520 cm^{-1} band is lower than that assigned to previous species of surface hydroxyl groups. Since perturbation on adsorption is small, this band may be due to some internal or interstitial hydroxyl group. Deuterium oxide adsorption at 300°C confirms this band to be due to a hydroxyl group, and not some combination or overtone mode. This band may be due to an OH vibration of a BOH group in some bulk phase of B_2O_3 (*25*). In addition, there is a possible connection with bands near 1733, 1640 and 1532 cm^{-1}, since these also increase on adsorption of water at high temperatures, suggesting some form of molecular water.

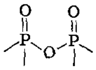
Mechanism of Water Adsorption

Since BPO_4 can be considered as a mixed oxide, many different sites involving P or B or both can be postulated to explain the reactivity and catalytic properties of boron phosphate. Boron phosphate used as catalyst, such as BP(RS-2) and BP(RS-3) is prepared with an excess of phosphoric acid, causing further complication. Also, the nominal P/B ratios for the high surface BPO_4 are based on the initial amounts of reactants used in the preparation, and an incomplete reaction may result in an excess of phosphorus since the more volatile tri-*n*-propyl borate will be more easily removed by evacuation (*26*). Experiments conducted in this laboratory indicated that evacuation at 700°C caused removal of some excess phosphorus probably in the form of phosphoric acid. Thus BP(TB-9,10α) with a nominal P/B ratio of 1.00 probably has an excess of P after evacuation at 300°C while the phosphorus decreases after 700°C evacuation.

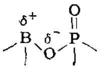
From the spectroscopic data, BP(TB-9,10α), BP(TB-11) and BP(RS-2,3α) appear to have a greater amount of phosphorus than boron on the surface. This phosphorus is likely in the form of a sheet-like $(PO_4)_n$ polymer, as suggested by Low (*19*) for phosphoric acid impregnated silica. The high boron BPO_4 appears to have an excess of boron on the surface, similar in properties to B_2O_3 on silica or porous glass (*18, 27*).

When freshly prepared, the high surface area BPO_4 samples are probably amorphous, as indicated by X-ray diffraction (*28*) and the broadness of infrared bands assigned to lattice vibrations. Narrowing of the bands on evacuation indicates that the boron phosphate becomes more crystalline when heated to higher temperatures. The changes in the structure also cause corresponding changes in the surface. Some infrared bands appearing on BPO_4 evacuated at 300°C cannot be regenerated by water adsorption on samples evacuated at 500 and 700°C. The surface area of BPO_4 reaches a maximum at about 350°C evacuation. The increase is probably caused by pores formed by escaping water. Presumably the BPO_4 contains a large number of internal OH's, condensed by evacuation about 300°C, this desorption being irreversible. Evacuation at 700°C results in another rearrangement, as the excess phosphorus desorbs as phosphoric acid.

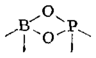
The spectroscopic work indicates that some water is dissociated on the surface, as indicated by the formation of surface hydroxyl groups. Previous work (*29*) also indicates indirectly the possibility of dissociated water on the BPO_4 surface. The band near 2800 cm^{-1} suggests  $\overset{\displaystyle O}{\overset{\|}{P}}\!\diagup OH$ groups are formed; or that  $\overset{\displaystyle O}{\overset{\|}{P}}$ groups are present on the surface. Further proof is provided by the behavior of a band near 1390–1385 cm^{-1}, that decreases on water adsorption. Corbridge (*30*) lists the band at 1368 cm^{-1} in P_2O_5 as due to P=O, and indicates this band is shifted by about 80 cm^{-1} by hydrogen bonding. However, Basila (*31*) has assigned a band at 1394 cm^{-1} appearing on silica alumina with similar properties as the BPO_4 band to a "strained" surface oxygen bridge (Structure III). Thus, there is some evidence of sites of the form



I

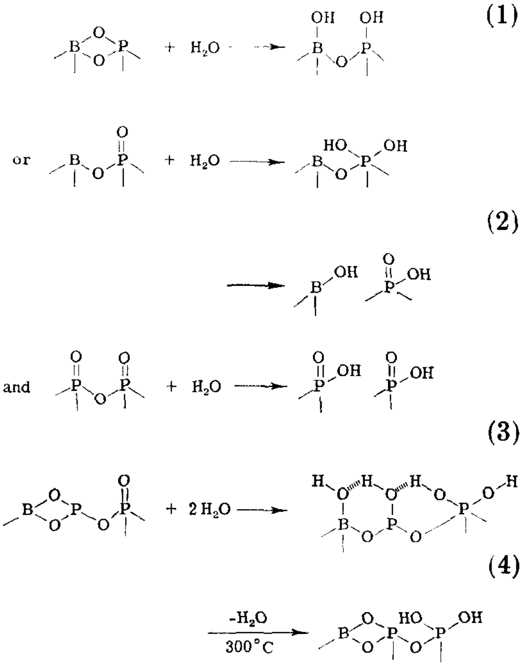


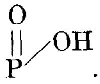
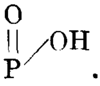
II

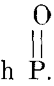


III

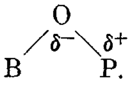
A number of dissociation reactions with water involving these groups can be postulated.



Possibly, dissociation reactions (1) result in the bands at 3595 and 3662 cm^{-1} (on water adsorption) assigned to BOH and POH. Hydrogen bonding may occur between these adjacent hydroxyl groups. Dissociation reactions (3) and (4) probably produce the  $\overset{O}{\overset{\|}{P}}\diagup OH$. For reaction (3), B–OH is also produced, but will also be strongly hydrogen bonded to the  $\overset{O}{\overset{\|}{P}}\diagup OH$.

The hydrogen bonded B–OH may be responsible for the band noted at 3300 cm^{-1}, although this is uncertain. Vicinal-OH groups may be produced; but may not be immediately noted if involved in hydrogen bonding, as in Eq. (5). When neighboring OH groups are removed by condensation, the less readily removed POH will appear. At this point, it should be noted that the surface structures indicated in the diagrams would suggest boron phosphate would have trymidite rather than cristobalite structure. Theoretically, a cristobalite structure would allow surface B–OH or P–OH, but not paired together. Exposed boron atoms are possible; but not paired with  $\overset{O}{\overset{\|}{P}}$. However, with the partially amorphous samples, the surface structure may differ. Similar results are observed for $AlPO_4$ (20), where paired Al–OH and P–OH groups were noted, even though the bulk structure is cristobalite. Possibly, localized distortions of the crystal structure allow paired B–OH and P–OH groups.

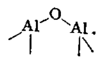
Although some water is dissociated by the BPO_4, some of the adsorbed water is probably not dissociated. However, the spectrum of water adsorbed on surface hydroxyls should be similar to molecular water, as for silica gel as example, with bands at 3400 and 1640 cm^{-1} (*32*). Similar bands are noted for BPO_4 only when large amounts of water are adsorbed. Thus, it is assumed that the band appearing near 2800 cm^{-1} is partially due to water strongly hydrogen bonded to the surface. This band decreases substantially for evacuation at room temperature; this would not be expected for dissociated water. Also, although the band near 1640–1650 cm^{-1} increases only slightly on adsorption, the percentage transmission in the 1800–1400 cm^{-1} decreases greatly on water adsorption, suggesting some strong broad overlaying band in this region. Van Wazer (*1*) suggests that B in BPO_4 is partially ionic with roughly one third a positive charge for each phosphorus atom, with the corresponding negative charge on the oxygen, i.e.,



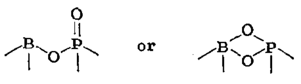
. This would mean the presence of dipoles on the surface. The negatively charged oxygens will probably form strong hydrogen bonds with water. Thus, some water would be dissociated on the BPO_4 surface, while some would be undissociated but strongly adsorbed on the surface; similar to "fixedly adsorbed" water on silica–alumina (*31*). Only for high surface coverage do bands appear assignable to loosely bound water. Investigations (*29*) of water adsorbed on BPO_4 also indicate that water is hydrogen bonded to surface oxides.

The spectroscopic investigations have shown that there are sites on the boron phosphate surface with a high affinity for water as well as sites capable of dissociating water.

There is no clear proof from the present work that these sites are responsible for the catalytic activity of BPO_4 for dehydration. However, the spectroscopic data appear to indicate that the surface of the high phosphorus BPO_4 sample is similar to alumina, rather than hydroxyapatite or aluminum phosphate. This is supported by earlier studies on the decomposition of ethanol on boron phosphate (*12*). The dehydration reaction of alumina has been explained in terms of "strained" oxide sites of the form



Possibly, the postulated



sites on BPO_4 may be directly or indirectly responsible for the catalytic activity of high phosphorus BPO_4 for dehydration reactions.

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