

Infrared Studies of Pyridine, 2,6-Dimethylpyridine, and 2,6-Di-*tert*-butylpyridine on Stoichiometric and Nonstoichiometric Boron Phosphate

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Received July 24, 1979

The adsorption of pyridine, 2,6-dimethylpyridine (26DMPy), and 2,6-di-*tert*-butylpyridine (26DTBPy) has been studied on stoichiometric and nonstoichiometric boron phosphate by infrared spectroscopy. It has been shown that boron phosphate with $P > B$ has a high percentage of Brønsted acid sites, while that with $P < B$ contains predominately Lewis acid surface sites. Both 26DMPy and 26DTBPy interact with Brønsted and Lewis acid sites, and both can be displaced, the latter more easily, by pyridine.

INTRODUCTION

The surface and catalytic properties of a variety of phosphates have been summarized in a recent review (1). Boron phosphate, in both stoichiometric and nonstoichiometric forms, has been the subject of a number of experiments in this laboratory. Recent work has employed isotopic exchange with H₂, D₂, and HD (2), temperature-programmed desorption (3), and the decomposition of alcohols (4, 5). It has been shown in these and earlier studies (1) that boron phosphate possesses acid sites, of both Brønsted and Lewis types, some of which are active in the decomposition of alcohols. Earlier work had employed infrared spectroscopy to study the surface of boron phosphate and the nature of the surface species formed on adsorption of ammonia and water (6). In the present work, the species formed with pyridine, 2,6-dimethylpyridine (26DMPy), and 2,6-di-*tert*-butylpyridine (26DTBPy) are examined spectroscopically in order to provide additional information on the nature and

strength of the acidic sites on the catalyst.

The adsorption of pyridine on a variety of catalysts has been studied by a number of workers. A summary of such results has been provided by Knözinger (7) for various oxides and by Benesi and Winquist (8) for a number of other catalysts. There are, however, no data available for pyridine or its derivatives on boron phosphate.

There is considerably less data available for the adsorption of derivatives of pyridine on solid surfaces than that which exists for pyridine itself. The adsorption of 4-methylpyridine and 2,4,6-trimethylpyridine (246TMPy) has been studied on δ -alumina with infrared spectroscopy by Knözinger and Stolz (9), who suggested that 246TMPy was chemisorbed through coordinate binding on Lewis sites. On the other hand, their experiments also showed that 246TMPy, although more basic than pyridine and 4-methylpyridine, is more weakly bound than these latter molecules. However, the use of 26DMPy as a proton-specific probe has been suggested by Benesi (10). Subsequently, Jacobs and Heylen (11), working with Y zeolites, found evidence to support the contention that 26DMPy reacts selectively with the hydroxyl groups.

Subsequently, Dewing, Monks, and

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Youll (12) showed that 26DTBPy can displace coordinately bound pyridine from alumina and postulated that at least part of the 26DTBPy is bonded to an electron-deficient oxygen species. Knözinger, Krietenbrink, and Ratnasamy (13) found no evidence, on $\gamma\text{-Al}_2\text{O}_3$, for interaction between hydroxyl groups and the nitrogen of 26DTBPy, and suggested that π bonds of the weakly adsorbed 26DTBPy may interact with the surface hydroxyl groups. However, these latter authors do support the contention (12) that 26DTBPy chemisorbs on exposed oxygen species.

26DMPy has also been employed in an infrared spectroscopic study of the surface properties of silica–magnesia gels (14) and of $\text{V}_2\text{O}_5\text{-MoO}_3$ both unsupported (15) and supported on MgO (16).

It thus seemed interesting to employ infrared spectroscopic techniques to study the interaction of various compositions of boron phosphate with three related substances of different basicities, namely, pyridine, 26DMPy, and 26DTBPy, to provide information on the nature and strength of the surface acid sites. At the same time, it was anticipated that the introduction of steric effects would allow further deductions concerning the structure of the surface of both stoichiometric and nonstoichiometric boron phosphate.

EXPERIMENTAL METHODS

Catalysts and Materials

Following the method previously described (6, 17) four sets of samples, BP12, BP10, BP9, and BP8, with phosphorus-to-boron atomic ratios 1.2, 1.0, 0.9, and 0.8, respectively, have been prepared. 26DTBPy and 26DMPy were obtained from ICN Pharmaceutical Company. 26DMPy was fractionated to remove water and pyridine and was distilled from silver nitrate to remove methylpyridines. Pyridine was from J. T. Baker Chemical Company and redistilled. All adsorbates were stored over a degassed 3A molecular sieve and were

degassed using several freeze–pump–thaw cycles prior to their use.

Infrared Studies

The boron phosphate sample (30–50 mg) was pressed into a disk 2.2 cm in diameter between two Teflon plates. The infrared cells were similar to those of Miyata *et al.* (18). The apparatus consisted of a conventional vacuum system, equipped with a mercury diffusion pump, a trap, a Pirani gauge, infrared cells, and a gas-dosing volume. The boron phosphate disk was subjected to outgassing treatment similar to those previously reported (6, 17). Generally, the temperature of the disk was slowly raised to 373 K and maintained for several hours. Afterward, the temperature of the cell was slowly raised to 723 K, and the sample was evacuated at this temperature for 10 h. It was then cooled to ambient temperature, and the ir spectra were recorded. Adsorbate of 270 or 50 Pa was introduced into the cell containing the sample and 30 min was allowed for the adsorption to reach equilibrium. The cell was then evacuated at ambient temperature and the temperature of the disk was raised. The spectra were recorded after adsorption and outgassing the sample at different temperatures. Infrared spectra were measured with a Perkin–Elmer 180 grating ir spectrometer carefully set to make instrument errors negligible. All infrared spectra were recorded with the sample at ambient temperature, nominally 298 K, but probably somewhat higher due to heating by the ir beam. A matched path length cell containing a similar boron phosphate disk was placed in the reference beam of the spectrometer in order to offset the background of the outgassed boron phosphate.

Gravimetric Measurements

Gravimetric studies were carried out on a Cahn electrobalance and with a quartz spring. The pressure was determined by means of a fused quartz precision pressure gauge from Texas Instruments. An 80- to

100-mg sample of boron phosphate which had been pressed into disks and broken into smaller pieces was used. Activation was achieved using the same procedures employed for the ir studies.

RESULTS AND DISCUSSION

Gravimetric Adsorption Studies

Table 1 summarizes the results of the gravimetric adsorptions. The third to fifth columns give the total number of molecules of pyridine or substituted pyridine adsorbed per square meter after evacuation for 30 min at 298 and 373 K. These values may include weakly and strongly adsorbed species.

Several features can be seen from an analysis of these data. The results for 26DTBPy indicate that 60–80% of the adsorbed material at 298 K is weakly bound. In general, it is seen that approximately 20–30% of the amount adsorbed at 298 K is desorbed at 373 K. The amounts adsorbed on BP10 show a maximum value for two of the three bases.

Infrared Spectra of Pyridine Adsorbed on Boron Phosphate

The effect of varying the phosphorus-to-boron ratio was investigated by infrared study in the region 1800–1400 cm^{-1} (Fig. 1). When sample BP12, previously treated under vacuum at 723 K, is allowed to adsorb pyridine and is then evacuated at cell tem-

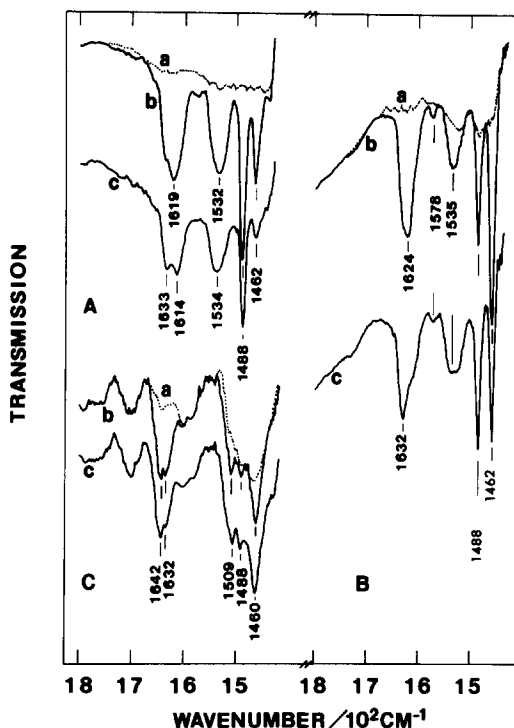


FIG. 1. Infrared spectra of pyridine adsorbed on boron phosphate. (A) BP12; (B) BP10; (C) BP9. (a) Background; (b) after introduction of pyridine (270 Pa), followed by evacuation for 30 min at cell temperature; (c) followed by evacuation for 30 min at 423 K.

perature, sharp bands at 1619, 1532, 1488, and 1462 cm^{-1} and very weak bands at 1578 and 1439 cm^{-1} are present (Fig. 1A(b)). At ambient temperature the presence of physisorbed pyridine is inferred from weak bands at 1439 cm^{-1} . When the desorption temperature is increased to 373 K, the intensities of these bands are reduced. At 423 K the band at 1619 cm^{-1} becomes two bands at 1633 and 1614 cm^{-1} , and the intensity of the 1462- cm^{-1} band decreases. The bands at 1532–1534 and 1462 cm^{-1} are characteristic of pyridinium ion and coordinated pyridine (19), respectively. Since the two bands at $1623 \pm 9 \text{ cm}^{-1}$ are strong these are tentatively suggested to be due to two types of pyridinium ions. However, Pohle and Fink (20), in their work with silica modified in one case with P_2O_5 and in another with B_2O_3 , have found, in both cases, a band at approximately 1625 ± 5

TABLE I

Adsorption of Pyridine and Alkylpyridines

| Reactant | <i>T</i> (K) | Adsorbed amount (10^{18} molecules m^{-2}) | | |
|----------|--------------|--|---------|--------|
| | | On BP12 | On BP10 | On BP8 |
| Pyridine | 298 | 1.97 | 2.81 | 1.53 |
| | 373 | 1.43 | 2.07 | 1.02 |
| 26DMPy | 298 | 1.80 | 2.02 | 1.67 |
| | 373 | 1.27 | 1.33 | 1.03 |
| 26DTBPy | 298 | 1.67 | 2.03 | 2.07 |
| | 373 | 0.65 | 0.47 | 0.60 |

cm^{-1} , which they assign to pyridine coordinated with a Lewis site.

In the case of BP10, analogous bands are observed (Fig. 1B). On evacuation at 423 K, only one band (1623 cm^{-1}) with a shoulder at 1616 cm^{-1} is observed, where two bands were found with BP12. On the other hand, on sample BP9, the band near 1535 cm^{-1} which is characteristic of pyridinium ion is not observed. In spite of the absence of the pyridinium ion, bands at 1642 and 1632 cm^{-1} are present, which may correspond to the "inner" and "outer" complexes which Knözinger (21, 22) suggested were formed by pyridine on the Lewis sites of alumina. The results show that the BP9 sample has only electron-acceptor centers which can coordinate with pyridine and that two types of coordinated pyridines are present. The results are summarized in Table 2. Such Lewis sites have been suggested previously (6).

It is possible to employ the ir spectra for pyridine on boron phosphate to estimate the numbers of Brønsted and Lewis acid sites on samples of various compositions, by using methods previously applied to silica-alumina catalysts. The ratio of the extinction coefficients for the 1462 (coordinated pyridine) and 1535 (pyridinium ion) cm^{-1} bands has been estimated previously for silica-alumina at values ranging from 1.1 to 3.5 (24-26). Unfortunately, the value of this ratio obtained for silica-alumina may differ from that applicable to boron

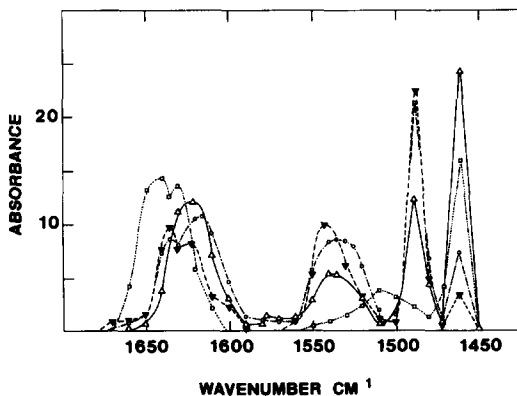


FIG. 2. Estimation of relative numbers of Brønsted and Lewis acid sites from infrared spectra of pyridine adsorbed on boron phosphate and on rehydrated boron phosphate. (a) BP12, \circ ; (b) BP10, Δ ; (c) BP10 rehydrate, \blacktriangledown ; (d) BP9, \square .

phosphate. However, as in the case of silica-alumina, the addition of water to boron phosphate converts Lewis acid sites to Brønsted species, as is evident from the disappearance of the 1462-cm^{-1} band and the intensification of the 1535-cm^{-1} band. The spectra obtained with BP10 before (Δ) and after (\blacktriangledown) addition of water were compared (Fig. 2). The peak areas found in Fig. 2 were employed to calculate the ratio of the absorbance for the 1462-cm^{-1} band relative to that of the 1535-cm^{-1} band as

$$A_{1462}/A_{1535} = 2.46.$$

Consequently, estimates of the relative amounts of Lewis and Brønsted sites were found from Fig. 2 (Table 3).

TABLE 2

Wavenumber $\bar{\nu}$ (cm^{-1}) of the Infrared Bands of Pyridine Adsorbed on Boron Phosphate

| PyH (On boron phosphate) | PyL | PyH (On P/SiO ₂) ^a | PyH (On AlPO ₄) ^b | PyL | Liquid Py | Vibrational mode |
|-----------------------------|-----------|--|---|------|-----------|------------------|
| 1632 | 1642 | 1640 | | | | |
| 1614 | 1632 | 1625 | 1615 | | 1580 | 8a |
| 1578 | | 1600 | 1582 | | 1572 | 8b |
| | | 1599 | | | | |
| 1540-1536 | 1462-1460 | 1537 | 1550 | 1451 | 1439 | 19b |
| 1488 | 1488 | 1497 | 1495 | 1495 | 1482 | 19a |

^a Reference (20).

^b Reference (23).

TABLE 3

| Sample | Apparent integrated intensity | | Acidity (%) | |
|--------|-------------------------------|------------|-------------|---------------|
| | A_{1582} | A_{1535} | Lewis site | Brønsted site |
| BP12 | 249 | 733 | 12.1 | 87.9 |
| PB10 | 873 | 395 | 47.3 | 52.7 |
| PB9 | 606 | — | 100.0 | 0.0 |

Infrared Spectra of 26DMPy Adsorbed on Boron Phosphate

Figure 3 shows the spectra of 26DMPy adsorbed on BP12 and BP9. After introduction of 26DMPy (270 Pa) to the cell containing BP12, spectra were recorded (Fig. 3b). On evacuation of the cell for 30 min at ambient temperature the bands at 1591 and 1578 cm^{-1} which are characteristic of liquid 26DMPy disappeared, while the bands at 1650, 1628, 1549, 1490, and 1463 cm^{-1} remained. The intensities of these bands re-

mained constant on increasing the adsorption temperature up to 523 K. The bands obtained with BP12 are compared in Table 4 with those obtained by Jacobs and Heylen (11) and Y zeolites. It is evident that, except for the 1549- cm^{-1} band, the spectra obtained with BP12 are in good agreement with those of the Y zeolites assigned to protonated 26DMPy. Although not shown in Table 4, this is also true of the relative intensities. Since protonated pyridine shows a band at 1550 cm^{-1} , it would be expected that a similar band would be observed with protonated 26DMPy. Although such a band was not observed by Jacobs and Heylen (11), a band at 1549 cm^{-1} was found by Dewing *et al.* (12). Kermarec *et al.* (14) displayed infrared spectra for silica-magnesia (18%) which showed a weak band at approximately 1650 cm^{-1} , as well as strong bands evidently due to both Brønsted and Lewis sites. The small band at

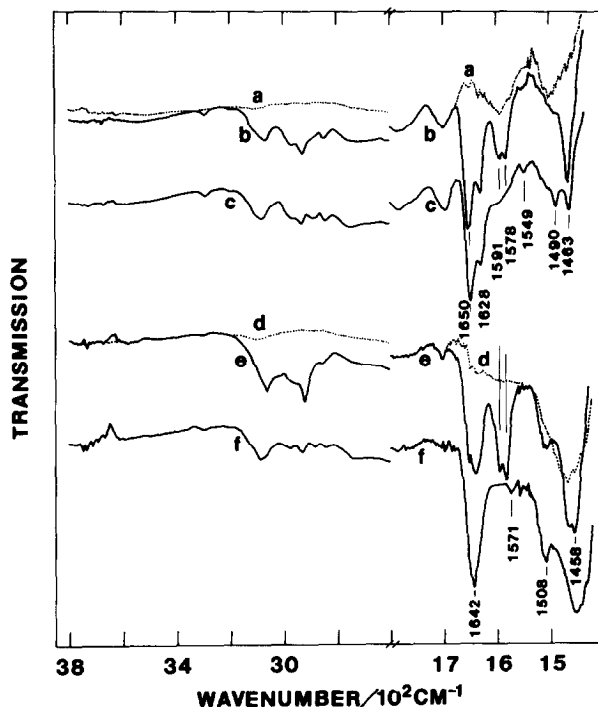


FIG. 3. Infrared spectra of 26DMPy adsorbed on boron phosphate. (a) Background (BP12); (b) after introduction of 26DMPy (270 Pa) at cell temperature; (c) followed by evacuation for 30 min at 373 K; (d) background (BP9); (e) after introduction of 26DMPy (270 Pa) at cell temperature; (f) followed by evacuation for 30 min at 373 K.

TABLE 4

Wavenumber $\bar{\nu}$ (cm^{-1}) of the Infrared Bands of 2,6-Dimethylpyridine Adsorbed on Boron Phosphate

| 26DMPyH (on boron phosphate) | 26DMPyL | 26DMPyH (on silica-magnesia) ^a | 26DMPyL | 26DMPyH (on zeolite) ^b | 26DMPyL | Liquid 26DMPy | Vibrational mode |
|---------------------------------|---------|--|---------|--------------------------------------|---------|------------------|---------------------|
| 1650 | 1642 | 1645 | 1605 | 1650 | 1603 | 1605 | 8a |
| 1628 | 1571 | 1630 | 1580 | 1630 | 1580 | 1580 | 8b |
| 1490 | 1508 | | | 1473 | 1477 | 1480 | 19a |
| 1463 | 1458 | | | 1452 | 1455 | | |
| 1549 | | | 1445 | 1415 | 1410 | 1410 | 19b |

^a Reference (14).^b Reference (11).

1549 cm^{-1} was tentatively assigned to protonated 26DMPy.

The results obtained for 26DMPy on BP9 (Figs. 3e and f); where the number of Brønsted sites is apparently small, provide an interesting contrast with those for BP12. From the figure, it can be seen that, although the intensities decreased on desorbing up to 523 K, none of the bands disappeared.

As compared to the frequencies on Y zeolites (11) and on silica-magnesia (14), coordinated 26DMPy on boron phosphate shows a larger frequency shift from that observed with liquid 26DMPy (11). With the Y zeolites (11), however, substantial frequency shifts of coordinated pyridine compared to pyridine in the liquid phase are observed. These frequency shifts and those observed with 26DMPy on boron phosphate may result from a charge perturbation in the pyridine ring and presumably reflect a strong coordination on the Lewis sites.

Infrared Spectra of 26DTBPy Adsorbed on Boron Phosphate

Infrared spectra of 26DTBPy adsorbed on sample BP12 showed several bands in the region 1700–1450 cm^{-1} as well as in the CH-stretching region (Figs. 4b and c and Table 5). On evacuation at ambient temperature for 30 min, the CH_3 asymmetric stretching vibration was displaced by 17 cm^{-1} toward a higher wavenumber as com-

pared to the liquid, and the band at 1575 cm^{-1} , due to weakly adsorbed or liquid 26DTBPy, disappeared. Even after evacuation at 373 K the shift is as high as 14 cm^{-1} . The shift of the CH_3 vibration to a higher wavenumber suggests that the CH_3 group interacts with the surface as reported by Knözinger (13). The bands remaining after evacuation at ambient temperature are still observed on evacuation at 373 K and are in agreement with those on silica-alumina reported by Dewing *et al.* (12) (Table 5). Therefore, it is concluded that 26DTBPy interacted with Brønsted acid sites on boron phosphate.

In the case of BP9, the band near 1528 cm^{-1} is not observed whereas the band at 1506 cm^{-1} , which was observed for coordinated 26DTBPy on alumina (12, 13) (Table 5), appears (Fig. 4e). For the BP10 sample (not shown), both bands at 1528 and 1506 cm^{-1} were observed. These results are in agreement with those obtained with pyridine as previously discussed. Consequently, it is concluded that, in spite of the steric hindrance of methyl groups, 26DTBPy interacts with both Lewis and Brønsted acid sites on boron phosphate.

Displacement of Adsorbed Species

Dewing *et al.* (12) have reported that 26DTBPy displaces pyridine previously adsorbed on alumina. However, Knözinger *et al.* (13) have been unable to observe such displacement behavior in ir spectra.

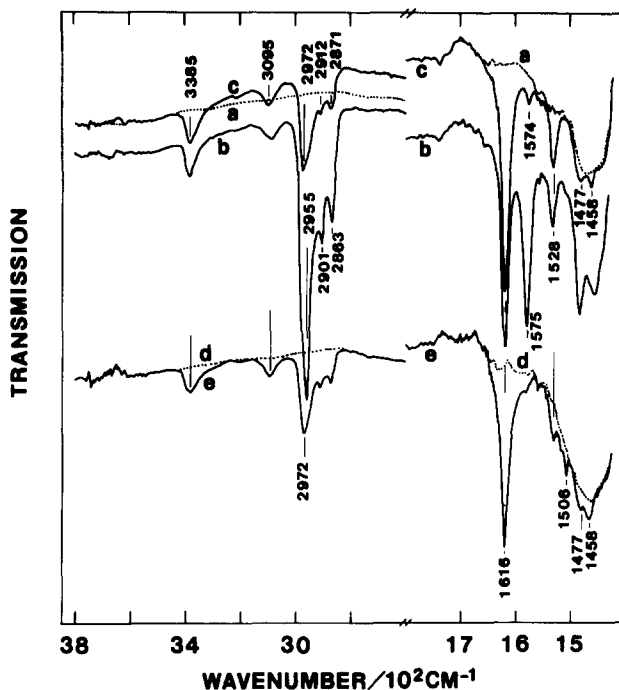


FIG. 4. Infrared spectra of 26DTBPY adsorbed on boron phosphate. (a) Background (BP12); (b) after introduction of 26DTBPY (50 Pa) at cell temperature; (c) followed by evacuation for 30 min at 373 K; (d) background (BP9); (e) after introduction of 26DTBPY (50 Pa) at cell temperature, followed by evacuation for 30 min at 373 K.

Pyridine (270 Pa) was introduced to a BP12 sample of boron phosphate on which 26DTBPY had previously been adsorbed. The bands at 2955, 2901, 2863, and 1575 cm^{-1} , which are characteristic of liquid 26DTBPY, as seen in Fig. 4b, were first

TABLE 5

Wavenumber $\bar{\nu}$ (cm^{-1}) of the Infrared Bands of 2,6-Di-*tert*-butylpyridine Adsorbed on Boron Phosphate

| 26DTBPYH (on boron phosphate) | 26DTBPYL (on boron phosphate) | 26DTBPYH (on silica- alumina) ^a | 26DTBPYL (on alumina) ^a | 26DTBPYL (on alumina) ^b | Liquid 26DTBPY |
|----------------------------------|----------------------------------|--|---------------------------------------|---------------------------------------|-------------------|
| 3095 | 3095 | | | 3095 | 3090 |
| 2972 | 2972 | | | 2977 | 2955 |
| 2912 | 2912 | | | 2918 | 2901 |
| 2871 | 2871 | | | 2880 | 2863 |
| 1616 | 1616 | 1615-1620 1625-1640 | 1615-1630 | 1620-1628 | |
| 1574 | 1574 | | | 1573 | 1577 |
| 1528 | | 1535-1545 | | | |
| 1477 | 1477 | 1470-1485 | 1470-1485 | 1482 | 1480 |
| 1458 | 1458 | | | 1455 | 1452 |
| | 1506 | | 1505-1510 1425-1430 | 1504 | |

^a Reference (12).

^b Reference (13).

observed. These bands disappeared on evacuation at ambient temperature, while the bands due to pyridinium ion and coordinated pyridine appeared. The results after evacuation at 373 K are shown in Fig. 5Ab. On BP9 samples of boron phosphate, where the interaction is primarily with Lewis acid sites, pyridine can again be seen to displace 26DTBPy (Fig. 5B). This behavior is in agreement with that observed by Knözinger *et al.* (13).

Experiments were also performed with samples of boron phosphate on which 26DMPy had previously been adsorbed (Figs. 5C and D). The introduction of pyridine to BP10 with chemisorbed 26DMPy produced small bands at 1540 and 1488 cm^{-1} (Fig. 5C). The results on BP9 are shown in Fig. 5D. In both cases, the dis-

placement of 26DMPy by pyridine appears to be relatively small.

Surface Acidity

In the present work three basic molecules, each with a similar local basic center, the pyridine nitrogen atom, but each differing in the substituents attached to the ring, have been examined. Ideally, it should be possible to gain further information on the distribution of surface acidic strengths for both Brønsted and Lewis sites. However, the differences in shape of the molecules considered introduce an additional factor, that of steric hindrance. The presence of both Brønsted and Lewis acid sites on two of the three catalytic compositions studied in this work adds a further difficulty to any attempt at assessing acidic strengths. The

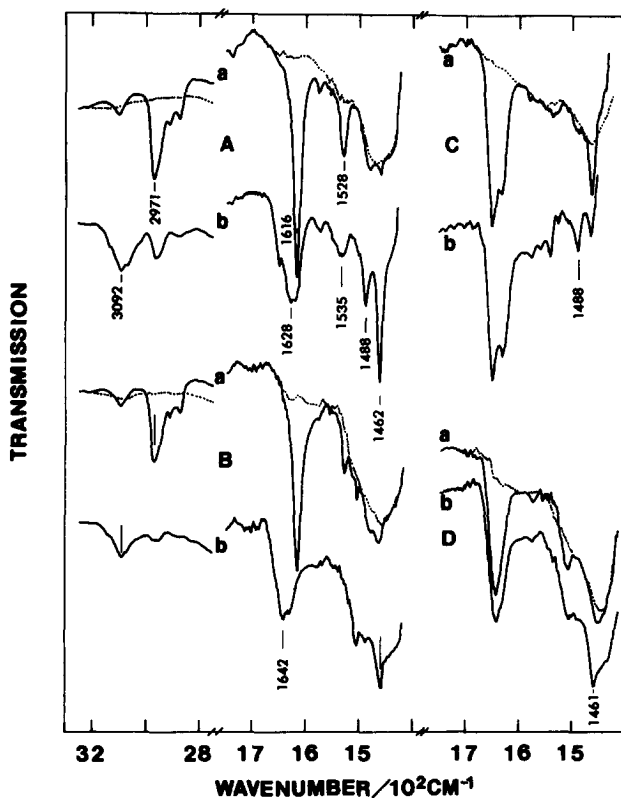


FIG. 5. Interaction of pyridine with 26DTBPy and 26DMPy adsorbed on boron phosphate. (A) BP12-preadsorbed 26DTBPy; (B) BP9-preadsorbed 26DTBPy; (C) BP10-preadsorbed 26DMPy; (D) BP9-preadsorbed 26DMPy. (a) After adsorption of 26DTBPy or 26DMPy at cell temperature, followed by evacuation for 30 min at 373 K; (b) after introduction of pyridine (270 Pa) at cell temperature on (a) followed by evacuation.

number of molecules remaining on the surface after evacuation at 373 K may be considered as the amount strongly chemisorbed while the difference between this quantity and that obtained after evacuation at 298 K may be taken as indicative of molecules relatively weakly bound to the surface. Since 26DMPy is a stronger base than pyridine, it would be anticipated that a larger quantity of the former than the latter would be held by the surface. However, from Table 1 it can be seen that the numbers of pyridine and of 26DMPy molecules chemisorbed on BP12 are approximately the same. This is also the case for BP8. This result may, at least in part, be due to the additional steric hindrance introduced by the two methyl groups. If the molecular area of pyridine is taken as $14.8 \times 10^{-20} \text{ m}^2$ (12), those of 26DMPy and 26DTBPy may be estimated at 19.2 and $44.2 \times 10^{-20} \text{ m}^2$, respectively. Inspection of Table 1 shows that the surface coverages, after evacuation at 373 K, are approximately 15–30, 20–26, and 20–30%, respectively. While these values cannot be exact, it appears that the relatively low values obtained for the amounts of 26DMPy adsorbed may be due, at least in part, to a surface-packing restriction. Thus, it is not possible to interpret, in any unambiguous fashion, the relative numbers of base molecules, remaining adsorbed after evacuation at 373 K, in terms of the concentrations and strengths of acidic sites.

Some further information can be obtained by noting (Table 1) the number of molecules per unit area removed on evacuation at 373 K. For pyridine and 26DMPy, these fall in the range of approximately $0.6 \pm 0.1 \times 10^{18} \text{ molecules/m}^2$; for 26DTBPy, the values are approximately twice as large. The unusual behavior of 26DTBPy in the gas and solution phases has been noted recently by various workers (27–30). Although 26DTBPy has a high gas-phase proton affinity, it is much less well solvated than would be expected (27). The hydrogen-bonding basicity of 26DTBPy, as found by measuring the equilibrium constant for

association with phenol, was only 0.52 compared to 38.5 and 69.2 for pyridine and 26DMPy, respectively (29). It was concluded that the *tert*-butyl groups must restrict the phenol complex so that even though the basicity increases as is evident from the proton affinity values, this is not observed in the hydrogen-bonding basicity. Further, the rate of protonation of 26DTBPy by the hydronium ion in solution is approximately 100 times slower than that of either pyridine or 26DMPy (30). The abnormally low basicity of 26DTBPy appears to be due to steric hindrance of solvation and not steric compression of the N–H bond in the protonated base.

From these results it then appears that, in spite of Brown and Bramer's original contention (31), the steric hindrance which apparently exists in the interaction of 26DTBPy with acidic molecules does *not* favor such interaction with Brønsted acids, but rather may actually hinder the association between hydroxyl groups, for example, and 26DTBPy. This appears to explain why, from the present infrared spectra, 26DTBPy does not discriminate between BP12, containing predominantly Brønsted acid sites, and BP9, containing largely Lewis sites. Since 26DTBPy has, on the basis of the solution-phase results, restricted ability to hydrogen bond, this may explain why such a relatively large quantity of 26DTBPy is desorbed at 373 K compared to that of pyridine and 26DMPy. In the cases of pyridine and 26DMPy, approximately 75% of these bases remain adsorbed after evacuation at 373 K, whereas with 26DTBPy, only approximately 30% is still held on the surface after such treatment. The relative ease with which pyridine displaces 26DTBPy, as compared with 26DMPy, is also indicative of the unusual behavior of 26DTBPy.

The present work has demonstrated that nonstoichiometric boron phosphate, where $P > B$, contains predominantly Brønsted sites, while that with $P < B$ is exclusively Lewis acidic in nature. This appears to be

qualitatively consistent with the accepted properties of boron and phosphorus. This also agrees with previous infrared studies of boron phosphate with ammonia and water (6). Studies of the decomposition of *n*-propanol on catalysts, where $P > B$, also suggested that such catalysts contained primarily Brønsted sites (4). It has been shown that up to 8×10^{18} molecules/m² of hydrogen atoms on the surface of these excess-phosphorus catalysts can be exchanged with deuterium (2). Temperature-programmed desorption experiments provided evidence for the loss of greater amounts of water weakly bound to the surface from excess-boron samples than from those containing excess phosphorus (3). Increase in the phosphorus-to-boron ratio from 1.0 to 1.4 increased the oxidation of iodide to iodine, a process expected to be catalyzed by Brønsted sites (3) and up to 28×10^{18} molecules/m² of ammonia has been shown to chemisorb on boron phosphate of various compositions (5).

The present results also show the existence of acidic sites of reasonably high strength on both high-boron and high-phosphorus samples. It has also been shown that 26DMPy and 26DTBPy are capable of binding to both Brønsted and Lewis acidic sites.

ACKNOWLEDGMENTS

One of us (J.B.M.) gratefully acknowledges the financial support of the National Research Council of Canada.

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