

## An Infrared Study of the Adsorption of Pyridine on Platinum and Nickel

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Infrared spectral data have indicated that pyridine dissociatively chemisorbs on silica-supported platinum forming a Pt-C  $\sigma$  bond at the "2" position and a coordinate bond with the nitrogen atom such that the molecule lies perpendicular to the surface. In the presence of HCl this is reversibly transformed into pyridinium chloride and with H<sub>2</sub> it is instantaneously hydrogenated to adsorbed piperidine. The latter does not appreciably desorb upon evacuation but dehydrogenates to reform chemisorbed pyridine. The same phenomenon occurs when piperidine is adsorbed on Pt/SiO<sub>2</sub> and confirms earlier speculation that adsorbed piperidine is mainly responsible for the poisoning of Pt during hydrogenation. Identical spectral features were observed when pyridine was adsorbed on supported Ir, Os, Rh, and Ru. On silica-supported nickel a different strongly adsorbed species is formed which has been identified as a simple nitrogen-coordinated pyridine which also lies perpendicular to the surface. As proposed by others, the coordination of pyridine on nickel can be promoted if the nickel had been pre-treated with O<sub>2</sub> or CO.

### INTRODUCTION

Pyridine has been used extensively as a probe molecule for determining the nature of the active sites on oxide catalysts (1, 2). By observing the infrared spectra of the adsorbed species in the 1700-1300 cm<sup>-1</sup> spectral region where the in-plane ring deformation modes and the CH deformation modes absorb, it has been possible to distinguish between adsorption centers which act as Lewis acid sites (coordinated pyridine), Brønsted acid sites (pyridinium ion formation), or as hydrogen-bonding sites.

Similar information can in principle be obtained by studying the adsorption on metals, although relatively few studies have

been carried out. Sheets and Hansen (3) have studied the adsorption of pyridine on oil-covered nickel and have found that chemisorption did not occur unless the nickel had been previously exposed to oxygen or carbon monoxide, in which case the pyridine was coordinately adsorbed. Primet *et al.* (4) studied the adsorption on alumina-supported platinum and found that in addition to the infrared bands which could be attributed to pyridine coordinately bound to the support, there were additional features which were due to a chemisorbed species on Pt. Their spectra were complex because of the overlapping bands due to the two types of adsorbed species, but they suggested that the adsorbed species on Pt was 2,2'-dipyridyl. However, their observation of a strong band at 1540 cm<sup>-1</sup> in the spectra of pyridine on Pt could also have conceivably been assigned to the pyridin-

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ium ion ( $pyH^+$ ) possibly as a result of interaction with adsorbed hydrogen on Pt.

The adsorption of pyridine has also been studied on nickel using ultraviolet spectroscopy (5) and on platinum using low energy electron diffraction (6, 7), and the hydrogen-deuterium exchange over both metals has been investigated by several workers (8-11). In these studies there seems to be general agreement that the nitrogen lone pair electrons of pyridine forms a coordinate bond with nickel such that the molecule lies perpendicular to the surface whereas on platinum a variety of adsorbed structures have been postulated. The above work will be discussed in detail below.

In view of the problems outlined above, we have undertaken a detailed investigation of the adsorption of pyridine on silica-supported platinum and nickel in order to determine the mode of adsorption on these

metals, whether the formation of a coordinated species can be promoted by the pre-adsorption of oxygen or CO on Ni, and to determine whether pyridinium ion formation takes place when pyridine reacts with surface hydrogen on Pt. A very brief examination of the adsorption on some other group VIII metals is also reported. The silica support was chosen because pyridine only hydrogen bonds to the surface hydroxyl groups of this material (1, 12).

## EXPERIMENTAL

Details of the techniques used for sample preparation and a description of the reaction cell (300-ml volume) have been published elsewhere (13). In the present work all silica-supported metal disks were 1 in. in diameter and contained 40 mg  $cm^{-2}$  of combined material. The weight percentage of metal was as follows: Pt(15.8), Ir(15.7), Rh(13.5), Ru(13.7), Os(12.6), and Ni(9.2). All spectra were recorded using a modified Perkin-Elmer model 13G filter-grating spectrometer and band positions were calibrated with reference to known band positions of gaseous species. Liquid pyridine- $h_5$  was dried by refluxing over  $CaH_2$  or  $LiAlH_4$  and pyridine- $d_5$  was used as received from Merck Sharp & Dohme of Montreal.

## RESULTS

### Platinum

When 10 Torr of pyridine was allowed to adsorb on to a silica sample which had been degassed at 300°C so as to remove physically adsorbed water, only the well-known infrared bands at 1597, 1487, and 1445  $cm^{-1}$  (Fig. 1A) due to hydrogen-bonded pyridine were observed (1, 12). This disappeared following evacuation for 24 h at 20°C or after 1 h at 50°C. When 10 Torr of pyridine was allowed to react with a Pt/SiO<sub>2</sub> sample, additional strong bands were observed at 1567, 1536, 1431, and 1410  $cm^{-1}$  (Fig. 1B) which persisted

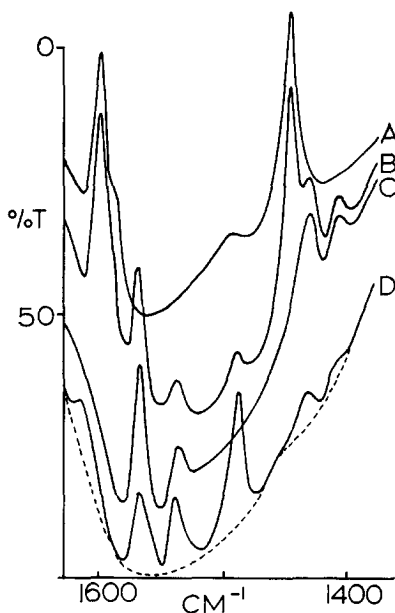


FIG. 1. (A) Infrared spectrum of adsorbed pyridine on a 40 mg  $cm^{-2}$  sample after degassing for 1 h at 20°C. (B) As for (A), but on a 40 mg  $cm^{-2}$  Pt/SiO<sub>2</sub> sample. (C) After evacuation of (B) for 1 h at 150°C. (D) After adding 1 Torr of HCl to (C). The dashed line in (D) shown how the background spectrum due to silica changes in this region. The %T scale refers to (D).

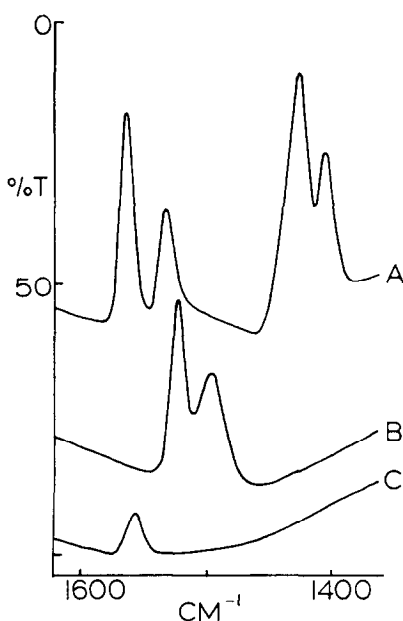


FIG. 2. (A) Infrared spectrum of chemisorbed pyridine on a compensated Pt/SiO<sub>2</sub> sample (compare with Fig. 1C). (B) As for (A) with pyridine-*d*<sub>5</sub>. (C) Infrared spectrum of adsorbed pyridine-*d*<sub>5</sub> on an oxygen pretreated Ni/SiO<sub>2</sub> sample. The %T scale refers to (B).

after removal of hydrogen-bonded pyridine by evacuation at 20°C or at 150°C (Fig. 1C). The only other new spectral features were three weak bands at 3072, 3040, and 3018 cm<sup>-1</sup>.

The silica background spectrum changes rapidly between 1650–1300 cm<sup>-1</sup> with maximum transmission near 1570 cm<sup>-1</sup> and zero transmission at 1330 cm<sup>-1</sup> (2). However, with a 40 mg cm<sup>-2</sup> SiO<sub>2</sub> disk in the reference beam of the spectrometer, a nearly level background spectrum can be achieved. A spectrum recorded under these conditions which is equivalent to that shown in Fig. 1B is shown in Fig. 2A. Figure 2B shows the equivalent spectrum of pyridine-*d*<sub>5</sub> adsorbed on a deuterated Pt/SiO<sub>2</sub> sample and has two bands at 1526 and 1500 cm<sup>-1</sup>.

The new bands are evidently due to a surface species which is strongly bound to the platinum and will hereafter be referred to as "chemisorbed pyridine." These bands did not diminish in intensity if the degas-

ing temperature was in the range 20–150°C, but at higher temperatures they decreased uniformly in intensity and disappeared after evacuation at about 300°C.

If a 5-μmole dose of pyridine was added (0.3 Torr), a weak spectrum of both H-bonded and chemisorbed pyridine was observed. Over a period of an hour (without evacuation) the bands due to hydrogen-bonded pyridine gradually disappeared and those of chemisorbed pyridine intensified. Evidently the chemisorbed species is formed preferentially.

The ratio of the intensities of the infrared bands due to chemisorbed pyridine did not alter when spectra were recorded with sample temperatures which ranged from -70 to +150°C (for initial reaction at 20°C) or if the reaction was carried out at 150°C. This, taken with the observations in the preceding paragraphs, suggests that a single chemisorbed species is formed.

Identical spectra of chemisorbed pyridine were obtained if pyridine had been allowed to chemisorb onto a hydrogen-covered Pt sample (i.e., one which had been cooled from 400°C in 400 Torr of H<sub>2</sub> and the H<sub>2</sub> had been evacuated for 5 min at 20°C) or on an essentially hydrogen-free sample (one which had been evacuated for 50 h at 400°C prior to cooling). The absence of a strong band near 1490 cm<sup>-1</sup> characteristic of the pyridinium ion (1, 14) indicated that this species is not formed. However, if 1 Torr (16 μmoles) of HCl was added, the spectrum shown in Fig. 1C immediately reverted to that shown in Fig. 1D. The 1567, 1431, and 1410 cm<sup>-1</sup> bands decreased in intensity, new bands appeared at 1620 and 1487 cm<sup>-1</sup>, and the 1536 cm<sup>-1</sup> band intensified. Pyridinium chloride has strong bands near 1620, 1540, and 1485 cm<sup>-1</sup> (1, 14), so we can infer that this or a closely related species was formed by a reaction between HCl and chemisorbed pyridine. Little spectral change occurred if the sample was evacuated at 20°C, but after evacuation for 2 h at 75°C the new

bands disappeared and the spectrum of chemisorbed pyridine was restored to within 15% of its intensity before HCl was added.

When H<sub>2</sub> was added to chemisorbed pyridine at 20°C, all bands immediately disappeared and were replaced by a pair of strong bands in the  $\nu(\text{CH})$  region at 2950 and 2865 cm<sup>-1</sup> and two broad weak bands at 1457 and 1520 cm<sup>-1</sup>. Little spectral change resulted following a brief evacuation of the H<sub>2</sub> at 20°C although a trace of piperidine was identified in a mass spectrometric analysis of the desorption products which could be trapped in liquid nitrogen. However, following 20 h evacuation of the H<sub>2</sub>, the new bands gradually diminished in intensity and those due to chemisorbed pyridine reappeared although they were less intense than those observed before H<sub>2</sub> was added. This process could be accomplished with 1 h evacuation at 75°C. An identical "new" spectrum was observed if piperidine alone was adsorbed on to a Pt/SiO<sub>2</sub> sample, and if this was evacuated at 75°C for 1 h, the spectrum also reverted to that of chemisorbed pyridine. Such reversible hydrogenation-dehydrogenation cycles have been previously noted for unsaturated hydrocarbons adsorbed on transition metals (15, 16), and we assume that the new bands can be attributed to chemisorbed piperidine.

If H<sub>2</sub> was added at 150°C, all infrared bands due to chemisorbed pyridine immediately disappeared and large quantities of *n*-pentane and ammonia were identified in a mass spectrometric analysis.

#### *Iridium, Osmium, Rhodium, and Ruthenium*

The identical set of bands were observed in the 1700–1400 cm<sup>-1</sup> spectral region when pyridine chemisorbed on any of the above metals. The band intensities with Ir and Os were as great as were observed with Pt, whereas they were about 10 times less intense for Rh and Ru. Since no specific metal surface areas were measured we are unable to quantitatively account for this

observation. In all cases the hydrogenation products were piperidine.

#### *Nickel*

A spectrum showing the bands at 1597, 1487, and 1445 cm<sup>-1</sup> due to hydrogen-bonded pyridine on a compensated 200-mg silica sample is shown in Fig. 3A. The spectrum observed following a similar adsorption sequence on a Ni/SiO<sub>2</sub> sample (45 min evacuation) is shown in Fig. 3B. Under these conditions some hydrogen-bonded pyridine is undoubtedly still present, but the weakest band is now centered at 1482 cm<sup>-1</sup> and it is relatively more intense than the corresponding band due to hydrogen-

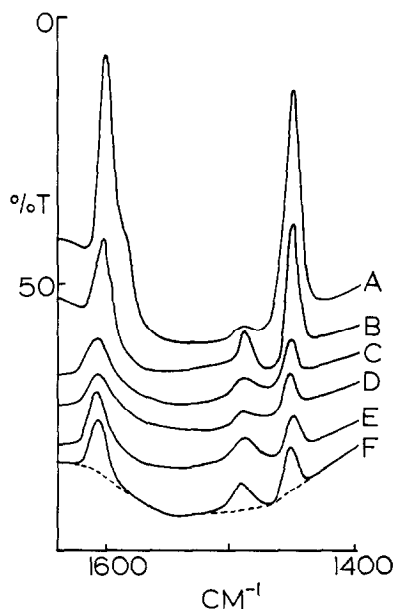


FIG. 3. (A) Infrared spectrum of pyridine adsorbed on a compensated 40 mg cm<sup>-2</sup> SiO<sub>2</sub> sample after degassing for 1.5 h at 20°C. (B) Infrared spectrum of pyridine adsorbed on a 40 mg cm<sup>-2</sup> compensated Ni/SiO<sub>2</sub> sample after degassing for 45 min at 20°C. (C) After degassing (B) for 18 h at 20°C. (D) After degassing (C) for 2 h at 100°C. (E) Pyridine adsorbed on oxygen-treated Ni/SiO<sub>2</sub> after evacuation for 14 h at 20°C, then for 1 h at 70°C. (F) Pyridine adsorbed on CO-treated Ni/SiO<sub>2</sub> after degassing for 18 h at 20°C (dashed line indicates background spectrum). The %T scale refers to (F).

bonded pyridine. Following evacuation under conditions which would ensure the removal of the latter (Fig. 3C or D), three bands remain at 1605, 1482, and 1447  $\text{cm}^{-1}$ . These bands decreased uniformly in intensity with higher temperatures of evacuation and disappeared after several hours degassing at 200°C. Accompanying this spectrum were weak bands between 3100–3000  $\text{cm}^{-1}$  which likewise disappeared at 200°C.

It is evident that a strongly adsorbed species is formed when pyridine interacts with bare nickel. Sheets and Hansen (3) reported that no adsorption occurred when pyridine interacted with oil-covered nickel films but that it did occur if the nickel had been pretreated with  $\text{O}_2$  or CO. To test this, partially oxygen- or CO-covered samples were prepared by allowing 200 Torr of  $\text{O}_2$  to react for 30 min with Ni/SiO<sub>2</sub>, or by allowing 0.45 Torr of CO to react for 5 min. Following the adsorption of pyridine and evacuation so as to remove hydrogen-bonded pyridine, the spectra shown in Fig. 3E (pre- $\text{O}_2$ -treated) and F (pre-CO-treated) were observed. The infrared bands due to adsorbed pyridine were always about twice as intense as those observed when using bare nickel. Finally, the spectrum observed when pyridine-*d*<sub>5</sub> was similarly adsorbed on an oxygen-pretreated sample (Fig. 2C) had a single sharp band at 1560  $\text{cm}^{-1}$ . As was reported by Sheets and Hansen (3) when preadsorbed CO was present, the  $\nu(\text{CO})$  bands shifted by about 70  $\text{cm}^{-1}$  to lower wavenumber.

No spectral changes were observed when 400 Torr of hydrogen was added at 20°C to a sample which contained adsorbed pyridine.

#### DISCUSSION

Identical spectral features were observed when pyridine reacted with platinum, iridium, osmium, rhodium, or ruthenium, and these were attributed to a single chemisorbed species. A very different spectrum was observed with nickel or with CO- or

oxygen-pretreated nickel, and for convenience this system will be discussed first.

#### Nickel

Sheets and Hansen (3) observed two bands at 1605 and 1450  $\text{cm}^{-1}$  in their infrared study of the adsorption of pyridine on oxygen- or CO-promoted nickel films which were suspended in a hydrocarbon oil. The 1450  $\text{cm}^{-1}$  band only appeared as a shoulder on the low wavenumber side of a hydrocarbon oil band at 1475  $\text{cm}^{-1}$ , which obscured any additional features in this region. They also observed four bands below 1350  $\text{cm}^{-1}$  (a region inaccessible to us) and assigned all new features to pyridine which was coordinated to the promoted nickel because of (a) an observed low wavenumber shift in the NiCO band which indicated that electron donation to the surface had occurred, and (b) all observed frequencies were very close to those in NiPy<sub>4</sub>(NCS)<sub>2</sub> which contains such an adduct. Support for this assignment came from their parallel study (3) of the ultraviolet spectrum of pyridine on Ni.

We can conclude that coordinated pyridine is also the adsorbed species observed in the present study. The same shift of the NiCO band was observed and, although we are restricted to the spectral range above 1350  $\text{cm}^{-1}$ , we have observed an additional band at 1482  $\text{cm}^{-1}$ . The major infrared bands in this region of all compounds containing coordinated pyridine are near 1605  $\text{cm}^{-1}$  (strong), 1485  $\text{cm}^{-1}$  (medium), and 1445  $\text{cm}^{-1}$  (strong), or there is a single strong band near 1560  $\text{cm}^{-1}$  for pyridine-*d*<sub>5</sub> (17–19). An identical pattern was observed here (Fig. 3). The only slight ambiguity is that the major bands for pyridine which is hydrogen bonded to the support are also near the values reported here, i.e., at 1597, 1487, and 1445  $\text{cm}^{-1}$ . However, we know that hydrogen-bonded pyridine can be removed after the degassing conditions employed (Fig. 3 C–F), a fact that was confirmed by observing that the broad strong band near

3000  $\text{cm}^{-1}$  due to hydrogen-bonded pyridine-HOSi groups had also disappeared from the spectrum. Further, independent experiments using  $\text{SiO}_2$  alone have shown that when the bands at 1597 and 1445  $\text{cm}^{-1}$  due to hydrogen-bonded pyridine are as intense as those shown in Fig. 3B, the band at 1487  $\text{cm}^{-1}$  has zero intensity (see also ref. 1). There can be little doubt that the band at 1482  $\text{cm}^{-1}$  in Fig. 3B is due entirely to coordinated pyridine.

A difference between our results and those of Sheets and Hansen (3) is that we have observed the same but weaker spectral features when pyridine is adsorbed on bare Ni/ $\text{SiO}_2$ . Kishi and Ikeda (5) also reported that pyridine formed a weak coordinate bond in their study of the ultraviolet spectrum of pyridine adsorbed on evaporated nickel. However, in view of our observation of enhanced intensity when pyridine was adsorbed on  $\text{O}_2$ - or CO-pretreated nickel, we conclude that the arguments advanced by Sheets and Hansen (3) regarding the promoted adsorption when a strong electron withdrawing species is already present on the surface are essentially correct.

Finally, the H/D exchange reaction (with  $\text{D}_2\text{O}$ ) over nickel powder in the liquid phase at 130°C has been studied by Calf *et al.* (8) who found that exchange was confined almost exclusively to the 2 and 6 positions in the ring. With 2-methylpyridine this exchange was severely deactivated and was completely deactivated with 2,6-dimethylpyridine (9). They suggested that pyridine adsorbed as a perpendicular ring with the nitrogen down, thus facilitating exchange at the *ortho*-positions, a process that was sterically unfavorable for the *ortho*-substituted pyridines. A similar conclusion was reached by Moyes and Wells (10) who likewise found that 2,6 exchange occurred almost exclusively at 42°C when  $\text{D}_2$  gas interacted with pyridine adsorbed on a nickel film. Both groups found that a greater degree of exchange occurred with Pt and suggested that a different type of

adsorbed species was present on this metal. Those results will be discussed below.

#### Platinum

Primet *et al.* (4) investigated the adsorption of pyridine on a partially CO-covered Pt/ $\text{Al}_2\text{O}_3$  surface. The band for PtCO was observed to shift from 2065 to 1990  $\text{cm}^{-1}$  as pyridine was adsorbed, and strong bands appeared in the 1650–1350  $\text{cm}^{-1}$  region at 1620, 1565, 1535, 1490, 1430, and 1405  $\text{cm}^{-1}$ . In a separate study of pyridine adsorbed on  $\text{Al}_2\text{O}_3$ , bands were found at 1620, 1576, 1490, and 1450  $\text{cm}^{-1}$  which were attributed to pyridine coordinated on alumina. The bands at 1535 and 1430  $\text{cm}^{-1}$  in the Pt/ $\text{Al}_2\text{O}_3$  spectrum were assigned to a 2,2'-dipyridyl species on the basis of a comparison with the spectral features of some metal complexes of this compound (4, 18, 20), a band at 1490  $\text{cm}^{-1}$  was attributed to pyridine on  $\text{Al}_2\text{O}_3$ , whereas the remaining bands at 1620, 1565, and 1450  $\text{cm}^{-1}$  were assigned to either pyridine on alumina or to 2,2'-dipyridyl on Pt. The 1405  $\text{cm}^{-1}$  band was unassigned. The choice of alumina as a support prevented Primet *et al.* (4) from making a definitive assignment. For example, coordinated pyridine on Pt would have bands at the same frequencies as those for pyridine on alumina, or the bands at 1620, 1535, and 1490  $\text{cm}^{-1}$  might equally have been assigned to a pyridinium ion (1, 14).

In the present work, the four infrared bands which were attributed to chemisorbed pyridine are at positions which are quite different from those to be expected for a simple coordinately bound molecule (1, 17, 18) or for a pyridinium ion (1, 14). The three low wavenumber bands coincide with bands assigned by Primet *et al.* (4) to a species on Pt, and we assume that our spectrum is the same as theirs but without the interfering bands due to pyridine on alumina. Like them, we observed a low wavenumber shift of the PtCO band after pyridine had chemisorbed on a surface that was about 10% covered with PtCO groups

prior to adsorption. [No chemisorption occurred if the surface was saturated with CO.] We can infer that charge is donated to the metal surface but that a simple coordinated species with the ring lying perpendicular to the surface is not present. We can further conclude that 2,2'-dipyridyl is not formed because of the absence of two expected strong bands, one near  $1600\text{ cm}^{-1}$  and the other in the  $1450\text{--}1480\text{ cm}^{-1}$  spectral region which are always present in the infrared spectra of coordinated 2,2'-dipyridyl (18, 20). We also note that the pyridinium ion or a closely related species was generated when HCl was added and not the 2,2'-dipyridylum ion (20) which has strong infrared bands at  $1600$ ,  $1500$ , and  $1432\text{ cm}^{-1}$ ; this suggests, but does not prove, that 2,2'-dipyridyl is unlikely to be present. Further, we note that although Raney nickel apparently catalyzes the formation of 2,2'-dipyridyl from pyridine at about  $100^\circ\text{C}$ , no such process has been reported for Pt (21). Moreover, in other recent studies of the adsorption (6, 7) and deuterium exchange (8-10) of pyridine on Pt (to be discussed further below), no evidence has been found which suggests that 2,2'-dipyridyl is formed.

In an attempt to further characterize the nature of chemisorbed pyridine, some additional experiments were conducted. These will be described below.

*Addition of  $\text{BF}_3$ .* When 1 Torr of  $\text{BF}_3$  was added to a sample which contained hydrogen-bonded and chemisorbed pyridine, the infrared bands due to hydrogen-bonded pyridine immediately disappeared but those due to chemisorbed pyridine were unaltered. Evidently the nitrogen

lone-pair electrons in the latter were unavailable for attack by this Lewis acid.

*Addition of  $\text{NH}_3$  or  $\text{H}_2\text{O}$ .* No displacement of chemisorbed pyridine resulted when 10 Torr of either of these was added.

*H/D exchange.* When pyridine- $d_5$  was added to a hydrogen-covered Pt sample (see Results section for preparation), the surface silanol groups instantaneously exchanged to become surface SiOD groups, and after several hours a very complex spectrum was observed in the  $1600\text{--}1400\text{ cm}^{-1}$  region indicating that mixed isotopic species were present. However, after reaction with a hydrogen-free sample, only a very slight degree of SiOH exchange occurred and there was no indication of the formation of mixed isotopic species; that is, a spectrum like that in Fig. 2B was observed. This SiOH exchange phenomenon is commonly encountered when hydrocarbons interact with silica-supported Pt (15, 16) and it is an indication that CH bond rupture occurred whereby the liberated surface deuterium subsequently exchanged with SiOH. Such exchange readily occurs when  $\text{D}_2$  is added to Pt/SiO<sub>2</sub>. Since SiOH exchange still took place on the essentially hydrogen-free surface, this probably indicates that dissociative chemisorption had occurred.

The above results, taken in conjunction with the observations noted earlier concerning the behavior of chemisorbed pyridine in the hydrogenation-dehydrogenation sequence, strongly suggest that the observed bands can be assigned to a monomeric cyclic  $\text{C}_5\text{N}$  species. Having ruled out a simple nitrogen coordinated species, the following structures might be reasonable:

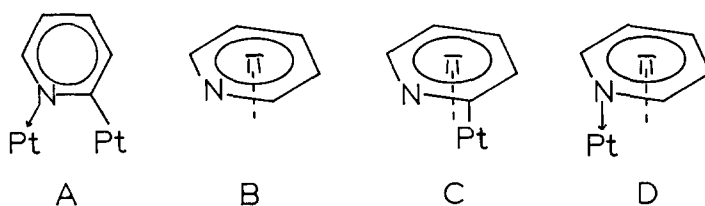


FIGURE 4

Structure A is proposed to lie "edge-on" with respect to the surface, i.e., perpendicular to the surface, whereas B, C, and D are assumed to be involved in  $\pi$  bonding via the ring system and lie flat. Structures A and C have a conventional Pt-C  $\sigma$  bond at the "2" position. The reasons for postulating bonding at this position are twofold. First, it is known that pyridine is a poison for platinum surfaces (21-23), yet 2,6-dimethyl pyridine is much less so (9, 22) which implies that the "2" position on pyridine has some special significance in connection with the mode of bonding. Second, exchange studies (8-10) have also indicated that the "2" position is very susceptible to exchange, a point which will be discussed further below.

Each of the structures above provide charge to the metal surface either by donation from the nitrogen atom or from the ring, and each of these could account for the observed low wavenumber shift of the PtCO band. Such a shift is known to occur when benzene is  $\pi$  bonded to Pt which contains preadsorbed CO (4). On the basis of the spectroscopic and chemical evidence so far discussed, it is not possible to definitively choose between these. However, structures C and D would appear unreasonable on steric grounds since the conventional bond with the surface (the Pt-C sigma bond in C or the Pt-N coordinate bond in D) would have to be at an appreciable angle with respect to the plane of the molecule. Of structures A and B, there are arguments which favor structure A.

(i) The two high wavenumber bands of liquid pyridine (1580 and 1572  $\text{cm}^{-1}$ ) are due to in plane ring deformation modes, whereas the two low wavenumber bands (1482 and 1439  $\text{cm}^{-1}$ ) are due to in plane CH deformation modes. The latter shift noticeably to lower wavenumber (24) when a heavy atom is substituted at the "2" position in the ring. It is conceivable that attachment of a surface Pt atom at this position might cause an even greater down-

ward shift. It is difficult to predict what shifts, if any, might result if pyridine was  $\pi$  bonded as in B. However, no  $\pi$  bonded sandwich-type compounds of pyridine exist.

(ii) There is evidence from our H/D exchange study that a small degree of dissociative chemisorption occurs. Moyes and Wells (10) studied the H/D exchange between gaseous  $\text{D}_2$  and gaseous pyridine over Pt powder at 100°C and found that exchange mainly occurred in the 2 and 6 positions with a lesser degree of exchange at other positions, and postulated that our species A played a dominant role in this process. [They also suggested that structure A was responsible for the 2,6 exchange for pyridine on nickel but could not convincingly rule out the possibility that a simple "addition-abstraction" mechanism solely involving coordinated pyridine on Ni was operative. This work has clearly shown that the structure of adsorbed pyridine on nickel is quite different from that on platinum.] Calf *et al.* (8) likewise found that slight exchange occurred at positions other than 2 and 6 for pyridine on Pt but suggested that the molecule was involved in both nitrogen coordination and ring  $\pi$  bonding to Pt such that the ring was tilted with respect to the surface, thereby facilitating exchange at other positions. We cannot conclusively rule this model out except that the degree of tilt might be expected to alter with temperature such that fairly obvious spectral changes would have been observed as the temperature was varied from -70 to +150°C.

(iii) Gland and Somorjai (6, 7) have recently carried out a low energy electron diffraction study of the adsorption of benzene and pyridine on Pt(111) and Pt(100) single crystal surfaces. They concluded from the LEED pattern and from the work function change on adsorption that benzene at low coverage laid flat on the surface and was  $\pi$  bonded via the ring system, whereas with pyridine, the ring lay perpendicular to the surface and charge



was donated via the nitrogen atom. Their data could not conclusively rule out our structure A and, indeed, they suggested that this was the structure if the adsorbed pyridine was heated to 250°C. There was no evidence that pyridine lay flat on the surface.

Although one has to be cautious in comparing the results from a LEED study on single crystal faces with the results obtained in an infrared study, we nonetheless believe that the LEED study strongly argues against our structure B. The only major point of difference in interpretation is that we can firmly conclude that a simple nitrogen-coordinated pyridine is not formed in our system. It may be that the near saturation surface coverages employed in this work favor processes which cause CH bond rupture [we note for example that adsorbed benzene changes from a predominantly  $\pi$  bonded structure to a  $\sigma$  bonded structure with increasing coverage (6, 7)]. Alternatively, our supported Pt catalyst undoubtedly has a relatively high step and kink density so that CH dissociation would be expected to be more favorable than on Pt(111) or Pt(100) surfaces (25).

In conclusion, we feel that the evidence argues strongly in favor of a model in which pyridine attaches itself to the platinum atom by forming a  $\sigma$  bond at the "2" position and a coordinate bond with the nitrogen lone pair electrons. Unsaturation is preserved and the molecule is presumed to lie perpendicular with respect to the surface.

#### CONCLUDING REMARKS

Pyridine and other nitrogen bases are notorious poisons for metal catalyzed hydrogenation reactions (22, 23). The present work has shown that a chemisorbed species of high thermal stability is readily formed on Pt. Freifelder (22) has shown that the "poison" is probably piperidine rather than pyridine itself. We would agree with this since we observed that chemisorbed pyridine was readily hydrogenated to adsorbed

piperidine. We do not know how the latter is attached to the surface but we do know that if piperidine itself is added to bare Pt the infrared spectrum is the same as is observed after adding H<sub>2</sub> to chemisorbed pyridine. In either case the adsorbed piperidine did not appreciably desorb following prolonged evacuation at 20°C. However, after evacuation at higher temperatures, adsorbed piperidine dehydrogenated to give chemisorbed pyridine. This suggests that the H/D exchange results of Moyes and Wells (10) might bear little relationship to the present work in that the active exchange sites probably occupy a small fraction of the "poisoned" surface.

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