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The Infrared Spectrum of Hydrogen Chemisorbed on Zinc Oxide

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Chemisorption of hydrogen on pure zinc oxide at 30°C produces bands at 2.86 and 5.85 μ which are attributed to oxygen–hydrogen and zinc–hydrogen stretching vibrations. The ratio of the intensities of these bands remains constant as the intensities of both bands increase with increasing hydrogen pressure up to 4 cm. Above a pressure of 4 cm, an excess of loosely bonded OH is observed. In addition to the covalent chemisorption which produces OH and ZnH bands, there is a slow chemisorption at 30° which does not produce detectable infrared bands. This slow chemisorption is attributed to H^+. When the zinc oxide is heated above 80° in hydrogen at constant pressure both bands decrease while again maintaining a constant ratio between OH and ZnH intensities. Above 80° an increase in the electrical conductivity is indicated by a decrease in the background transmission. It is concluded that the irreversible change in conductivity is due to reduction of the zinc oxide. It is also concluded that the high temperature maximum which is commonly observed for hydrogen–zinc oxide isobars is not due to formation of an OH species.

INTRODUCTION

In early studies of hydrogen on zinc oxide (*1*) isobars were observed which had adsorption maxima near 80° and 150°C. Although the double maxima isobars are not observed for hydrogen on some doped zinc oxides (*2*) and the relative heights of the maxima can be modified by exposing zinc oxide to hydrogen at high temperatures (*3*), it is generally accepted that the double maxima isobars are characteristic for hydrogen on pure zinc oxide. In previous work much effort has been devoted to arriving at an understanding of these double maxima isobars. The work of Wicke (*4*), who attributes the low temperature maximum to hydrogen chemisorbed on zinc atoms and the high temperature maximum to hydrogen chemisorbed on oxygen atoms, is of interest with regard to the work to be discussed here because this suggestion is amenable to direct testing by the infrared method.

The hydrogen-on-zinc-oxide system has also been the object of many studies which were stimulated by the fact that the conductivity of zinc oxide may be increased by chemisorption of hydrogen (*2, 5, 6, 7*). These studies have led to the conclusion that there is one type of hydrogen chemisorption occurring below 100°C which does not affect the conductivity of zinc oxide and another type of chemisorption at high temperatures which increases the conductivity. In the present paper attempts are made to relate the observations of the infrared studies to the conductivity effects. It has been shown that the transmission of zinc oxide is an inverse function of the conductivity (*8–11*), so that it is possible to obtain a qualitative measure of conductivity changes by observation of changes in the background transmission of the sample.

EXPERIMENTAL METHOD

The general method used for obtaining the infrared spectrum of hydrogen on zinc

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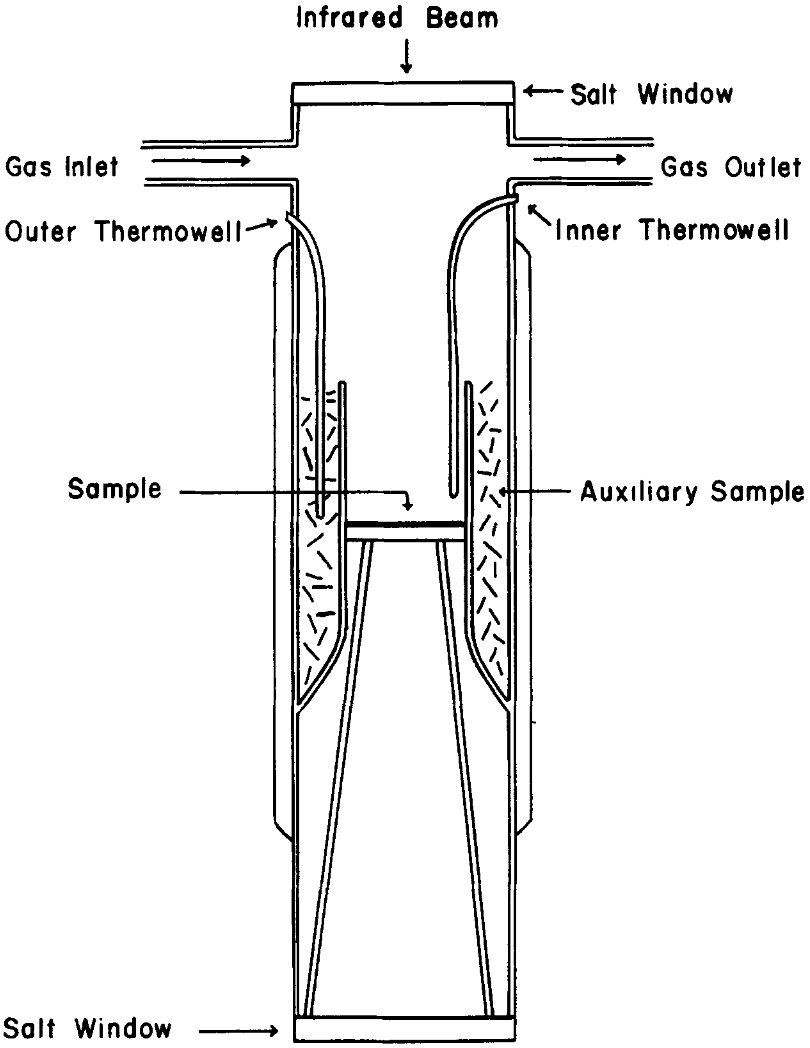

FIG. 1. Infrared cell with auxiliary sample chamber.

oxide was similar to that described for other chemisorption systems (*12*). The sample cell was modified in order to place an auxiliary sample in a space between the regular sample and the cell wall as shown in Fig. 1. Use of an auxiliary sample was necessary to obtain a quantitative measure of the volume of hydrogen chemisorbed because the dead space of the cell was large. The auxiliary sample weighed 86 g and the regular sample weighed 0.70 g. The regular sample was used in the form of a disk, 26 mm in diameter, obtained by pressing in a die at 25,000 psi (*13*). The auxiliary sample was pressed into disks of the same size and weight as the regular sample. It was assumed that the volume of hydrogen chemisorbed per unit weight was the same for the regular and auxiliary samples. The use of the auxiliary sample in the manner illustrated in Fig. 1 suffers the disadvantage of poor temperature distribution, causing the inner thermocouple reading to be as much as 30° lower than the outer during pretreatment procedures involving evacuation near 400°C. Because of the temperature distribution difficulty no attempt was made to measure the volume of chemisorption in the infrared cell at temperatures above 30°C. Ancillary measurements of the chemisorption of hydrogen at higher temperatures were made in a conventional chemisorption apparatus. The ancillary measurements showed that the 30°C difference in pretreatment temperature cannot be used to support the argument that slow chemisorption occurs only on the auxiliary sample and thereby explain the failure to observe bands attributable to hydrogen taken up by the slow chemisorption process.

A filter, prepared on a CaF_2 window by the Bausch and Lomb Optical Company of Rochester, New York, which cuts off the radiation below 2.3 μ, was inserted between the sample and the Globar. This filter was used to minimize heating of the sample by the infrared beam and to avoid the possibility of the zinc oxide being activated by the high energy components of the beam. Because the possibility of zinc oxide being affected by the radiation is itself of interest, other experiments were conducted with the filter removed. No affect attributable to the zinc oxide being modified by the short wavelength radiation was observed.

The zinc oxide was Kadox-25 obtained from the New Jersey Zinc Company of New York, New York. This zinc oxide has a mean particle diameter of 1100 Å and its surface area is 10 m^2/g. The supplier lists its purity as 99.7% with 0.27 of the remaining 0.3% being water. The data reported in Figs. 2, 3, and 4 were obtained with the previously mentioned sample disk which weighed 0.70 g. The data reported in Figs. 5 and 6 were obtained with a disk weighing 0.75 g. An auxiliary sample was not used with the latter disk. Prior to chemisorption of hydrogen the zinc oxide was evacuated at pressures of 10^{-4} mm for three hours at a sample disk temperature of 350°C. Chemisorption experiments carried out in a separate apparatus confirmed that Kadox-25 shows the common double maxima isobars.

The intensity values plotted in Figures 3, 4, and 6 were obtained by multiplying the optical density times the half-width expressed in cm^{-1}. Observations of the band found near 2.86 μ were made with a spectral slit width of 14 cm^{-1}. The half-width of this band ranged from 22 to 26 cm^{-1}. Observations of the band near 5.85 μ were made with a spectral slit width of 4.8 cm^{-1}, the half-width of this band ranging from 10 to 13 cm^{-1}. A Perkin-Elmer spectrometer, equivalent to a Model 12C, fitted with a CaF_2 prism was used for the reported work. The transmission of the 0.75 g sample was 17% at 4 μ prior to addition of hydrogen.

Determination of the amount of water produced by reduction of zinc oxide was made by circulating palladium-diffused hydrogen (20 cm) over 85 g of zinc oxide and freezing the water into a liquid nitrogen trap. The water was reacted with calcium carbide to form acetylene and the acetylene determined by mass spectrometric analysis.

RESULTS AND DISCUSSION

Hydrogen on Zinc Oxide at Low Temperature

Chemisorption of hydrogen at 30°C and pressures near one-half atmosphere produces new bands at 2.86 μ and 5.85 μ. Bands typical of those observed under these conditions are shown as spectrum A of Fig. 5. The band at 2.86 μ is attributed to the oxygen–hydrogen stretching vibration of OH groups. The band at 5.85 μ is attributed to the zinc–hydrogen stretching vibration of ZnH or $(ZnH)^+$ groups. The latter assignment is primarily based on analogy with the zinc–hydrogen stretching band of gaseous zinc hydride which has been reported at 6.2 μ (*14*). In the present discussion no attempt is made to distinguish between ZnH and $(ZnH)^+$. In other experiments, which will not be discussed in detail here, chemisorption of hydrogen produces an additional small band at 5.95 μ. It is possible that the difference between ZnH and $(ZnH)^+$ is represented by the difference between the 5.85 and 5.95 μ bands.

Prior to chemisorption of hydrogen there are bands in the OH stretching region which have not been removed by the 350°C evacuation. These background bands remain constant during the experiments to be discussed here. It is not clear whether these bands are due to surface OH groups or to OH groups within the bulk of the zinc oxide. Figure 2 shows details of the OH stretching region and is intended to show how the OH bands produced by chemisorption of hydrogen are distinguished from the OH bands of the background.

In Fig. 2 the solid line, A, is the background observed prior to chemisorption. The solid line, B, is observed after adding one-half atmosphere of deuterium. This produces a new band at 3.84 μ, attributed to OD, without producing a change in the OH bands of the background. The dashed line, curve C, was observed after reducing the deuterium pressure to a few mm and adding one-half atmosphere of hydrogen. In this case the resulting spectrum, C, is superimposed on A. Again, as in the case of deuterium adsorption, no effects attributable to changes in the bands originally present in A are detected.

Chemisorption of deuterium also produces a band, attributed to ZnD, at 8.12 μ. The isotope shift ratios of 1.34 and 1.39 are reasonable for the OH and ZnH structures which have been postulated.

Before assignment of the 5.85 μ band to the zinc–hydrogen vibration, consideration was given to the possibility that the 2.86 μ band represents an oxygen–hydrogen stretching vibration and the 5.85 μ band represents an oxygen–hydrogen bending vibration. On the basis of the accumulated experience with OH vibrations of conventional compounds it is unlikely that an OH species could produce a sharp stretching band at 2.86 μ and an intense OH bending band at 5.85 μ. However, it has been shown that in special cases strong hydrogen bonding can displace an OH bending vibration into the 5.9 μ region (*15*). Because the detection of ZnH is of critical interest to studies of the surface chemistry of zinc oxide, support for this assignment was obtained from exchange experiments. In these the behavior of the 2.86 and 5.85 μ bands, first observed with 10 cm of hydrogen, was followed after the pressure was increased to 40 cm by addition of deuterium at 30°C without removing the hydrogen. The 2.86 μ band decreased to the equilibrium value in about one hour. The exchange was much slower for the 5.85 μ band and after 18 hours this exchange was only about halfway to equilibrium. This marked difference in the rate of exchange shows that both bands are not produced by the same spe-

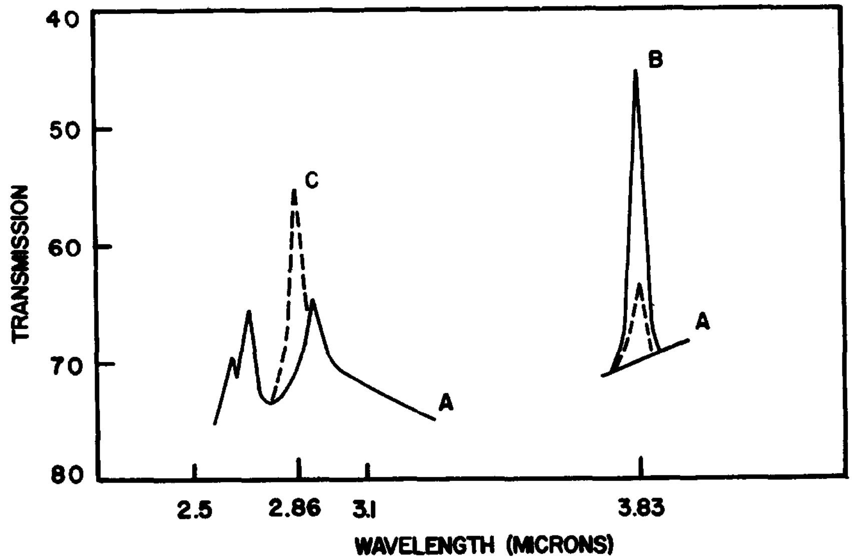

FIG. 2. Hydrogen and deuterium on zinc oxide at 30°C. A—Background after evacuation at 350°C. B—With one-half atmosphere of deuterium. C—With one-half atmosphere of hydrogen (plus small amount of deuterium).

cies. The possibility that there are two OH species—one which produces an OH stretching band but no detectable bending band, while the other produces a bending band but no detectable stretching band—is too unlikely to merit serious consideration. Thus, the deuterium exchange experiments provide strong support for the assignment of the 5.85 μ band to a zinc–hydrogen stretching vibration.

The possibility of detecting physically adsorbed hydrogen, by a band near 2.4 μ (*16*), or the molecule-ion H_2^+, by a band near 4.6 μ (*17*), was also considered in the present work, but no bands attributable to these species were observed. Thus, as in the case of hydrogen on platinum (*18*), the bands observed during the infrared study of hydrogen on zinc oxide provide no evidence for hydrogen chemisorbed without rupture of the hydrogen–hydrogen bond.

The intensities of the bands in Fig. 2 are partially dependent on the amount of hydrogen chemisorbed, and the amount chemisorbed is a function of the hydrogen pressure. The chemisorption of hydrogen on zinc oxide is complicated by a slow chemisorption process, so the amount adsorbed is also a function of the time of exposure. The slow chemisorption will be discussed in connection with Fig. 4. Figure 3 is based on spectral measurements that were completed within 15 min after the specific pressures were attained. The chemisorption which produces the bands on which Fig. 3 is based is easily reversible and evacuation at 30°C causes the bands to disappear.

Figure 3 was obtained by plotting the intensity of the OH band against the intensity of the ZnH band as the hydrogen pressure was increased at 30°C. Starting at zero, the points in Fig. 3 represent bands observed at pressures of 0.1, 0.35, 2.3, 5.2, 13.0, 38.7, 114, 232, and 507 mm. This figure shows that there is a linear relationship between the OH and ZnH intensities over the major portion of the curve, and that the linear portion passes through zero.

On the basis of this linearity it is concluded that there is a constant ratio in the number of OH and ZnH groups formed by the chemisorption process represented by this portion of the curve. It is reasonable to assume that this constant ratio is unity, and that the chemisorption process being observed results from a splitting of hydrogen molecules by zinc–oxygen pairs on the surface,

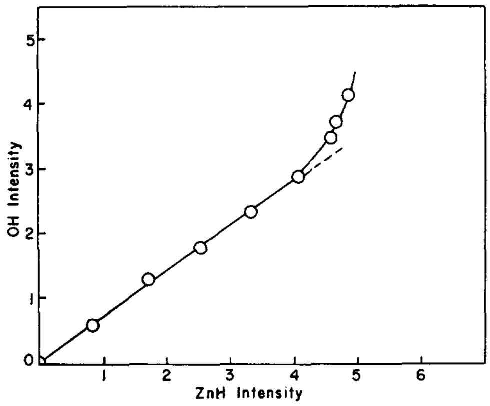

FIG. 3. Plot of the intensity of the OH band versus the intensity of the ZnH band with increasing pressure at 30°C.

$$ZnO + H_2 \rightarrow ZnH + OH$$

At high intensities the curve breaks away from the straight line in a manner indicating that more OH's than ZnH's are being formed. This change will be discussed later.

Figure 4 was obtained by plotting the intensity of the OH band and the intensity of the ZnH band as functions of the amount of hydrogen chemisorbed at 30°C. For simplicity this figure may be divided into three sections. In the first section neither OH nor ZnH bands are detected although there are 0.03 cc/g of chemisorbed hydrogen. In the second section both the OH and ZnH bands increase linearly. The third section represents chemisorption that proceeds with only small increases in the band intensities.

Starting at the common point of zero intensity for a chemisorption of 0.01 cc/g, the eight points designated by circles on each curve were observed at the hydrogen pressures of 0.1 to 232 mm which appear in Fig. 3. The point which represents a pressure of 507 mm in Fig. 3 does not appear in Fig. 4 because the volume of hydrogen chemisorbed was inadvertently not measured at that pressure.

In another experiment on the same sample, after desorbing previously adsorbed hydrogen by evacuation at 350°C, the volume of hydrogen chemisorbed increased from 0.17 to 0.26 cc/g when the system was allowed to stand for 16 hr at 30° with a hydrogen pressure of 50 cm. The data obtained at the start and end of this 16 hr period are indicated by squares in Fig. 4. Despite the 50% increase in the volume chemisorbed, the ZnH intensity remained constant while the OH intensity increased by only 14%.

From Fig. 4 it is evident that, in addition to the hydrogen chemisorption which produces OH and ZnH bands, there is a type of hydrogen chemisorption on zinc oxide which does not produce detectable bands. This species is assumed to be H^+. It is obviously difficult to support structural assignments which must be based on the failure to detect bands. However, as in the case of hydrogen on nickel, where chemisorption occurred without detection of nickel–hydrogen bands (*18*), the H^+ interpretation appears to be the most reasonable of the possible alternatives.

This H^+ is visualized as being ionically bonded to the surface and shared between three surface oxygen atoms. Such a species is not expected to produce a detectable infrared band in the 2.3–8.3 μ region which was scanned in the present experiments. It would probably produce a broad, shallow band at longer wavelengths.

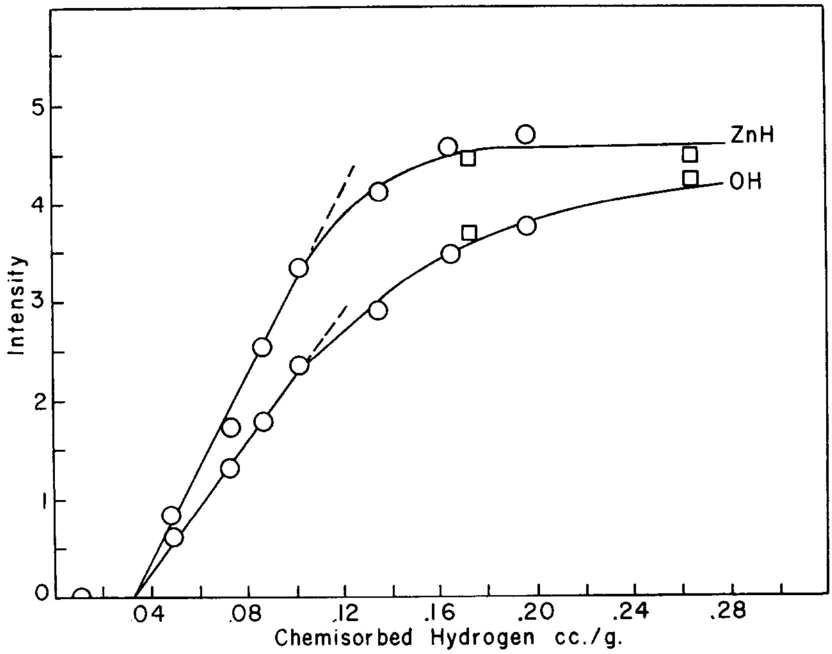

FIG. 4. Plots of the OH and ZnH intensities as functions of the volume of hydrogen chemisorbed at 30°C.

On the basis of 1.1×10^{19} zinc and oxygen atoms per square meter of surface it is estimated that zinc oxide having an area of 10 m^2/g could absorb about 4 cc/g by the mechanism, $H_2 + ZnO \rightarrow ZnH + OH$. Thus, the maximum adsorption of 0.27 cc/g in Fig. 4 represents only a small fraction of the maximum amount predicted by calculations based on simple geometrical concepts. A much larger volume of hydrogen adsorbed on zinc oxide has been measured at liquid nitrogen temperature (*1*) and was attributed to physical adsorption. There is a possibility that the adsorption at liquid nitrogen temperature is a weakly bonded chemisorption which would produce ZnH or OH bands. No infrared work has been done to test this possibility.

Figures 3 and 4 show that several types of hydrogen chemisorption on zinc oxide at 30°C must be considered. On the basis of the amount chemisorbed the most important of these are the slow chemisorption which does not produce detectable bands, and the covalent chemisorption which produces equal amounts of ZnH and OH. The situation is complicated by the slow adsorption which produces "excess OH" in the third section, and the rapid adsorption of the first section of Fig. 4 which does not produce detectable bands. In subsequent discussion the chemisorption of the first section of Figure 4 will not be considered separately but will be considered as a special form of the "slow" ionic chemisorption.

Figure 4 shows that there may be as many as four different types of hydrogen chemisorption on zinc oxide at 30°C. Despite this complexity one important point is clear: none of these types of hydrogen chemisorption produces an increase in the conductivity of the zinc oxide at 30°. This is shown by the fact that there is no significant change in the background transmission of the sample over the experimental sequence shown in Fig. 4. This result is consistent with previous work in which the conductivity of zinc oxide was measured by conventional methods (*2, 5, 6, 7*).

Hydrogen on Zinc Oxide at High Temperature

Three general mechanisms for the increase in conductivity of zinc oxide, produced by exposure to hydrogen at high temperature, will be considered in subsequent discussion. The first, which will be referred to as the "hydroxyl" mechanism, visualizes chemisorption as providing conduction electrons by the reaction (*19*),

$$H_2 + 2O^{2-} \rightarrow 2OH^- + 2e$$

Another version of the hydroxyl mechanism attributes the enhancement of conductivity to the production of easily ionized excess zinc atoms (*20*),

$$O^{2-}Zn^{2+}O^{2-} + H_2 \rightarrow Zn^\circ + 2OH^-$$
$$Zn^\circ \rightarrow Zn^+ + e$$

The hydroxyl mechanism predicts an increase in the number of OH groups at higher temperatures.

The second mechanism, which will be designated the "proton" mechanism, is based on the concept that conduction electrons are provided by the route (*21*),

$$H_2 \rightarrow 2H \rightarrow 2H^+ + 2e$$

In the discussion of Fig. 4 it was assumed that the slow chemisorption which does not produce detectable bands is due to chemisorption of hydrogen as protons. Thus, to be consistent with the present work, the proton mechanism must be modified to account for the fact that the slow chemisorption does not increase the conductivity at 30°. This modification has been anticipated by the concept that at low temperatures the electron is held in traps (*22*). These traps could be zinc atoms or Zn^+ ions. The proton mechanism, coupled with the assumption that chemisorbed protons do not produce detectable infrared bands, implies that the adsorption responsible for the high temperature maximum of the Taylor and Strother isobars would not produce new bands.

The third mechanism is based on the idea that the increase in conductivity is caused by a "reduction" reaction which leaves easily ionized excess zinc atoms on the surface. This differs from the hydroxyl mechanism in that the oxygen is removed as water,

$$ZnO + H_2 \rightarrow Zn + H_2O\uparrow$$

Since the sample was warmer than other parts of the system, the infrared methods used in the present studies would not be reliable as a means of detecting desorbed water. The experiments designed to determine the amount of water produced, which are discussed later, were undertaken to remedy this deficiency.

The consensus of those who have studied the chemisorption of hydrogen on zinc oxide by conventional volumetric methods is that the reduction mechanism cannot play an important role in work carried out below 300°C. This belief is supported by the fact that apparently the entire volume of chemisorbed hydrogen may be recovered (*1*). However, Thomas and Lander (*6*) have suggested the reduction mechanism to account for their observation that the conductivity did not decrease to its 150°C value when their sample was cooled to 150° from 300°C.

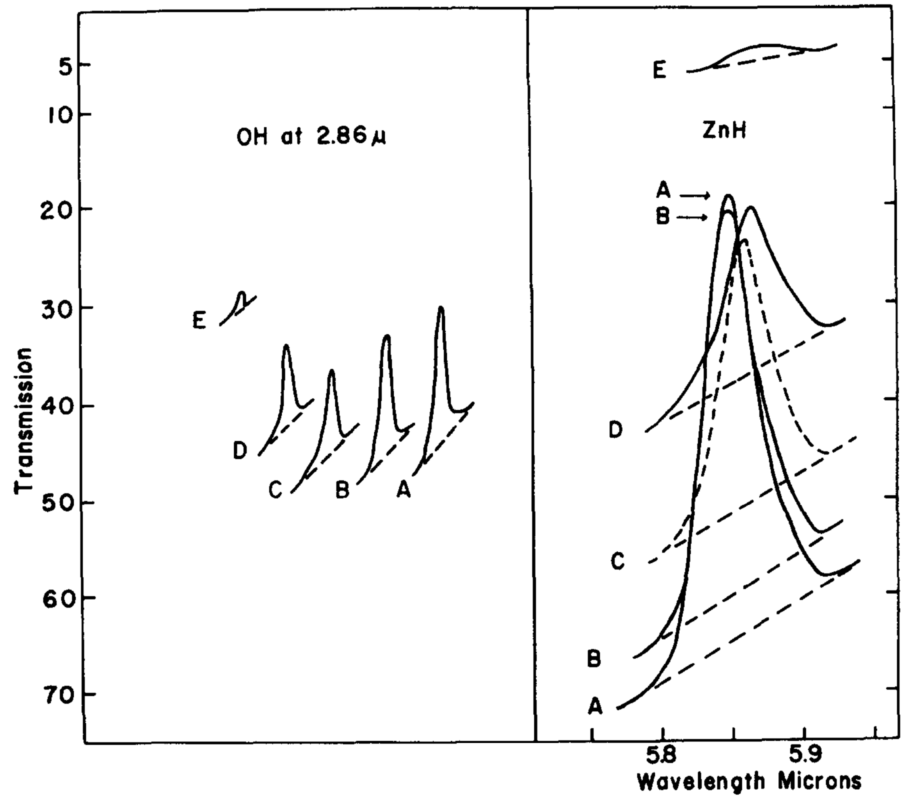

FIG. 5. Effect of increasing temperature on the OH and ZnH bands at a hydrogen pressure of 40 cm. A at 30, 40, and 60°C; B at 80°C; C at 100°C; D at 120°C; E at 130°C.

Figure 5 shows the effect of increasing temperature on the OH and ZnH bands. The bands were first observed after exposing a 0.75 g sample of zinc oxide to 40 cm of hydrogen at 30°. The sample remained in the hydrogen atmosphere as the temperature was raised. This is considered to be a constant pressure experiment although there were minor increases in pressure (1–2 cm) due to the heating of a portion of the closed system.

In Fig. 5 spectrum A of the ZnH region represents bands observed at 30°, 40°, and 60°C. There is no significant change in background transmission or band intensity over this temperature range. Spectrum B, observed at 80°C, shows a slight decrease in band intensity and a slight decrease in background transmission (i.e., the conductivity has increased). Spectrum C at 100°C, and D, at 120°C, show progressively greater decreases in band intensity and background transmission, and *E*, at 130°C, shows only a small residual ZnH band.

In the OH region it is also possible to represent the spectra at 30°, 40°, and 60° by a single spectrum, A. Spectrum B at 80° shows a decrease in band intensity but only a small change in transmission. The decreases in transmission and intensity become progressively greater as shown by spectrum C at 100°C, spectrum D at 120°C, and spectrum E at 130°C. Since there is only a small change in transmission in the OH region, the wavelength scale has been shifted for ease of presentation. All of the bands in the OH region were observed near 2.86 μ. Part of the change in transmission shown in Fig. 5 is reversible and part is irreversible. When the sample is cooled to room temperature after being heated to 130°C, the transmission falls to the level observed at 80–100°C in Fig. 5.

In another experiment the temperature was increased to 160°C. At this temperature the ZnH region is opaque. However, there was sufficient transmission in the OH region to permit the observation that there was no detectable OH band. In order to circumvent the difficulty caused by low transmission at high temperatures, a very thin ZnO sample (0.02 g cm^{-2}) suspended in a platinum gauze was studied using a Perkin-Elmer Model 21 spectrophotometer fitted with a scale expander. At 160° under conditions similar to those of the previous experiments, no bands attributable to OH or ZnH were detected. These observations will be considered as an extension of Fig. 5.

Figure 6 is similar to Fig. 3 in that it shows a plot of the OH intensity versus the ZnH intensity. For Fig. 6, however, the bands were observed with increasing temperature at constant pressure, while for Fig. 3 the bands were observed with increasing pressure at constant temperature. The conductivity did not change during the sequence represented by Fig. 3, but increased as the band intensities decreased during the sequence represented by Fig. 6.

In the interpretation of Fig. 6 it is assumed that the 130°C point (E) is not reliable. Then, rejecting (E), it is possible to draw Fig. 6 with a straight-line segment that is similar to that of Fig. 3. Moreover, as in Fig. 3, the curve deviates from the straight line in the direction of relatively more OH groups at high intensity values.

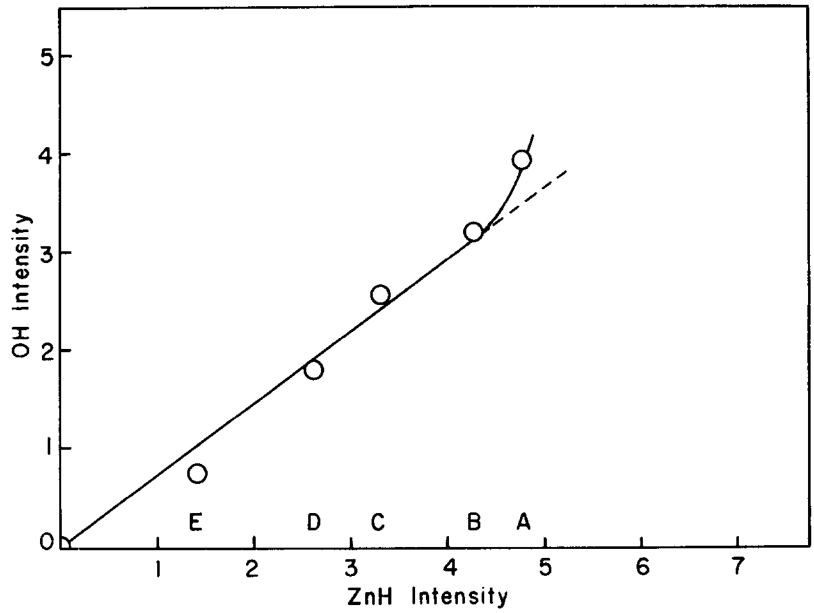

FIG. 6. Plot of OH intensity versus ZnH intensity. A at 30, 40 and 60°C; B at 80°C; C at 100°C; D at 120°C; E at 130°C. Hydrogen pressure, 40 cm.

Figures 5 and 6 support one of the basic conclusions of the present work, namely, that the increase in adsorption at high temperature is not accompanied by an increase in the number of OH groups. The excess OH groups observed at room temperature represent a relatively unstable species which is desorbed by heating to 80°C. Thus, the excess OH species cannot be responsible for the high temperature maximum in the isobars.

It is easier to draw conclusions with respect to the isobars than it is for the changes in conductivity. The isobars involve all of the hydrogen which has been taken up while it is necessary to consider the possibility that the conductivity changes may be produced by only a small part of the chemisorbed hydrogen.

If it could be assumed that the chemisorption which affects the conductivity proceeds by the same mechanism which produces the high temperature maximum in the isobar, the hydroxyl mechanism could be ruled out for both effects. With the above assumption the reduction mechanism could also be ruled out for both effects since the idea that the high temperature maximum represents hydrogen going to produce water is not consistent with previous results which indicate that the chemisorbed gas can be recovered as hydrogen (*1*). The proton mechanism is consistent with the available evidence when modified by the concept of election trapping at room temperature to explain the absence of changes in conductivity under this condition. Thus the assumption that the two effects are directly related would lead to a relatively clear-cut decision in favor of the proton mechanism.

However, there is evidence that the above assumption is not correct and that only a small part of the high temperature hydrogen is involved in the conductivity change. Thomas (*8*) has provided a plot of the transmission of ZnO sheets as a function of the number of charge carriers. Comparison with his data indicates that the Kadox-25 has 2×10^{17} carriers per cc of ZnO prior to addition of hydrogen. After heating in hydrogen to 130° and cooling to room temperature the Kadox-25 has gained an additional 2×10^{17} cc^{-1} or 3.5×10^{16} g^{-1}. This gain could be provided by the chemisorption of 0.0013 cc of H_2 per gram of ZnO on the basis of one carrier per molecule of chemisorbed hydrogen. The order of magnitude of this estimate of the minimum quantity of chemisorbed hydrogen needed to produce the observed conductivity effect, is supported by the fact that the increase in conductivity can be reversed by chemisorption of 0.0045 cc g^{-1} of O_2. The measured chemisorption of hydrogen after heating to 130° is about 0.4 cc g^{-1}. It is evident that the minimum quantity of chemisorbed hydrogen needed to produce the increase in conductivity could be about two orders of magnitude smaller than the volume chemisorbed at the high temperature maximum of the isobar.

A study of the amount of water produced by reduction of Kadox-25 at 160° and the behavior of the bands due to excess hydroxyl in Fig. 6 provide evidence that the irreversible change in conductivity observed in the present experiments is due to reduction. After circulating hydrogen for 4 hr over Kadox-25 at 160°C, the quantity of water involved was 0.008 cc g^{-1}. The amount of reduction did not increase above this level for experiments at temperatures up to 280°C. At 300°C, 0.03 cc g^{-1} were produced and above 300° the amount of water was greater than the limits anticipated in calibration runs and was not determined. At room temperature 0.0005 cc g^{-1} was detected. It is evident that there is a reduction plateau between 160° and 280° which is sufficient to account for the observed changes in conductivity. The minimum temperature of this plateau has not been determined by reduction experiments but the behavior of the excess hydroxyl band suggests that it might extend to temperatures as low as 80°C. The relatively small amount of hydrogen involved in the reduction makes it likely that this loss of hydrogen would not have been detected in the gas recovery experiments (*1*).

The excess hydroxyl in Figs. 3 and 6 represents 0.5–0.7 intensity units. Comparison with the straight line portion of Fig. 4 indicates that this intensity is equivalent to that produced by chemisorbing 0.02 cc of hydrogen with each molecule of hydrogen producing one hydroxyl. This quantity of hydroxyl would produce water to the extent of 0.01 cc g^{-1} by the reaction,

$$2\text{ZnOH} \rightarrow \text{ZnO} + \text{Zn} + H_2O$$

or 0.02 cc g^{-1} by the reaction,

$$\tfrac{1}{2}H_2 + \text{ZnOH} \rightarrow \text{Zn} + H_2O$$

Either of these values is close enough to the 0.008 cc g^{-1} produced in the reduction experiments to suggest the possibility that the excess hydroxyl represents a species which is an intermediate in the reduction and is desorbed as water. The band due to excess hydroxyl cannot be attributed to adsorbed water since the latter produces an OH band at 2.73 μ rather than 2.86 μ. The behavior of the band due to excess hydroxyl suggests that the reduction which affects the irreversible change in conductivity is complete when the excess hydroxyl disappears at 80°C. This concept receives support from the fact that the transmission falls to the 80–100°C level when the zinc oxide is cooled to 30° after exposure to hydrogen at 130°.

On the basis of the evidence discussed above it is concluded that the irreversible change in conductivity produced by heating zinc oxide in hydrogen to 160°C, is due to a reduction mechanism similar to that proposed by Thomas and Lander to explain observations in the 150–300° range. This conclusion implies the mechanism which affects the conductivity is basically different from the mechanism which accounts for the major portion of the adsorption at the high temperature maximum of the isobar. As previously stated, the latter is clearly due to a species which does not produce detectable infrared bands. This species has been tentatively identified as protons. The protonic adsorption which is responsible for the high temperature maximum in the isobar occurs to a limited extent at room temperature as a "slow chemisorption." The low temperature maximum of the isobars appears to be due to the superposition of the reversible covalent adsorption which produces ZnH and OH bands onto increasing quantities of slowly chemisorbed hydrogen. Above the first maximum the covalent adsorption decreases faster than can be compensated for by the increasing slow chemisorption. The minimum around 80–100° represents the point at which the decrease in covalently adsorbed molecules is balanced by the increase in protonic adsorption.

Infrared studies of the chemisorption of oxygen, water, chlorine, carbon monoxide, and carbon dioxide on zinc oxide were carried out concurrently with the studies of chemisorbed hydrogen. [The results with carbon monoxide and carbon dioxide were similar to those reported by Taylor and Amberg (*23*)]. The results obtained with these gases will not be discussed in detail here because they are not directly relatable to the hydrogen work. However, it must be mentioned that oxygen adsorption on zinc oxide prepared by heating zinc oxalate under vacuum for 16 hr at 350°C produced a series of bands in the 4–6 μ region. These bands appear to be related to carbonaceous impurities, but their significance has not been fully assessed. Zinc oxide samples which produce these bands do not produce bands on exposure to hydrogen, but heating in oxygen above 400° modifies the impure zinc oxide so that the 2.86 μ and 5.85 μ bands of chemisorbed hydrogen can be obtained.

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