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Hydrogen Activation on Zinc Oxide

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Three types of hydrogen adsorption have previously been characterized on zinc oxide at low temperatures, designated Types I, II and III. One of these, Type III, is a molecular form of adsorption which can be specifically titrated by nitrogen adsorption on 10–20% of the surface with formation of a molecular nitrogen species. This selective titration by a molecular nitrogen adsorption was employed to study the participation of molecularly adsorbed hydrogen in the allotropic (ortho-para) hydrogen conversion and isotopic (H_2–D_2) hydrogen exchange. The promotional effect of oxygen on the conversion reaction was also investigated. These results at low temperatures clearly indicate that the conversion reaction proceeds predominantly by a molecular paramagnetic mechanism involving this type III hydrogen below 140°K, while the exchange reaction proceeds via a Bonhoeffer–Farkas mechanism involving type I hydrogen at both low temperature and also at room temperature. At low temperatures, the exchange and conversion reactions are independent, but this is not necessarily true at room temperature. A mathematical model is presented for the paramagnetic conversion based on Wigner's theory involving longer times of interaction. The result is an enhancement of the conversion rate by several orders of magnitude with the deuterium conversion being enhanced more than the molecular hydrogen conversion.

INTRODUCTION

Heterogeneous catalysts that are effective for hydrogenation reactions usually are also effective for isotopic exchange and allotropic (ortho–para) conversion of hydrogen (*1*,*2*). The exact nature of the "activated" hydrogen in these sequences has been the subject of much speculation (*3*,*4*). Bonhoeffer and Farkas (*5*) originally proposed a dissociative mechanism to explain both the allotropic conversion as well as isotopic exchange. During hydrogenation the atomic hydrogen would undergo stepwise addition to adsorbed olefins to form the product alkanes. Although the model of the "active" hydrogen involving only an atomic adsorbed species can account for many features of the hydrogenation and exchange reactions, there are some deficiencies in this view. This model was modified by Rideal (*6*) [and later Eley (*4*)] to account for these deficiencies. In the proposed sequence it is assumed that exchange and conversion occur via reaction of the adsorbed atomic hydrogen species with molecular hydrogen (or deuterium). Twigg (*7*) presented a parallel mechanism for hydrogenation involving the addition of molecular hydrogen to an adsorbed olefin. This form of molecular hydrogen is often assumed to be weakly adsorbed. Little evidence has been presented to distinguish conclusively between these two mechanisms for isotopic exchange.

Wigner (*8*), as well as Kalckar and Teller (*9*), has proposed a theory for allotropic conversion by collision of hydrogen with a paramagnetic gas molecule. Farkas *et al.* (*10–13*) applied this theory to the heterogeneous catalytic exchange by paramagnetic sites on a catalytic surface. The interaction of hydrogen with a paramagnetic surface site and the resulting model of the molecule as a hindered rotor was

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[1] Editor's note: The joint research described in this article was prepared for publication by Dr. W. C. Conner following the death of Professor R. J. Kokes in 1973.

discussed by White and Lassettre (*14*) and later refined by King and Benson (*15*). This was used to explain the chromatographic separation of allotropic and isotopic hydrogen. Recently, Van Cauwelaert and Hall (*16,17*) has investigated and suggested the possible modifications of the conversion theory by collision to include the hindered rotor model of hydrogen interaction with a resulting enhancement of the para-conversion rate. An attempt was made to investigate the validity of this combined mechanism.

Although infrared studies provide convincing evidence for atomic adsorption of hydrogen on some metals (*18,19*) and oxides (*20*), evidence for chemisorbed molecular hydrogen is less certain. For years the strongest nonmechanistic evidence for chemisorbed molecular hydrogen stemmed from measurements of the isosteric heats of adsorption (*2*), but more recently, studies of the chromatographic separation (*17,22,23*) of the isotopes and allotropes of hydrogen have strongly supported this view. Moreover, the low temperature infrared spectra of Kokes *et al.* (*24–25*) have provided direct evidence for the existence of chemisorbed molecular hydrogen on zinc oxide.

Hydrogen adsorbs on zinc oxide in two forms (Types I and II) at room temperature (*26*) and in a third form (Type III) at 78°K (*27*). Type I hydrogen adsorbs rapidly and reversibly to yield ZnH and OH bands in the ir at room temperature by dissociation on a limited number of zinc oxide pair sites (*20,24*). At room temperature, saturation, estimated by both isotherms and ir band intensities, is approached at 50 mm pressure of hydrogen with a surface coverage of about 10%. This adsorption exhibits a pronounced kinetic but no equilibrium isotope effect (*28*). As the temperature is reduced to 78°K, these band intensities change very little. Type I hydrogen is also the reactive form for ethylene hydrogenation. Ethylene inhibits isotopic exchange and, in the hydrogenation reaction with hydrogen isotopes, their gas phase molecular identity is preserved on addition (*29*).

Type II adsorption occurs rapidly initially, but slowly in latter stages and continues at an observable rate for several days (*24,20–33*). No ir bands attributable to Type II hydrogen are found even though the extent of Type II adsorption is about twice that of Type I. The structure of Type II hydrogen is uncertain. Type II hydrogen neither reacts with ethylene nor exchanges rapidly with reacting hydrogen during hydrogenation of ethylene, yet either Type II H_2 or D_2 serves to promote the rate of hydrogenation at room temperature by about 30% (*28*). The presence of Type II hydrogen on a zinc oxide surface in the presence of dry oxygen at room temperature promotes poisoning of the catalyst by the water formed (or by its precursor), an effect not found in the absence of Type II hydrogen (*24*).

Type III hydrogen is evident at temperatures near 78°K. Infrared ir bands are found at 4019, 3507 and 2887 cm^{-1} for molecularly adsorbed H_2, HD and D_2, respectively. There is an inverse equilibrium isotope effect with a ratio of molecular deuterium adsorbed to molecular hydrogen adsorbed at constant pressure of about 1.2:1. Maximum surface coverage is about 10%, and there is strong evidence that this molecular adsorption occurs on the same sites that effect Type I chemisorption (*26,27*).

The interactions of oxygen and nitrogen adsorbed at 78°K with the pair sites on zinc oxide (and the hydrogen adsorbed on these sites) are different (*34*). Oxygen adsorbs nonspecifically with a constant isosteric heat of adsorption, whereas nitrogen is, to some extent, specific with an initially higher heat of adsorption up to a surface coverage of 10–20%, beyond which it decreases to a value close to that for oxygen. The effect of adsorbed water on the Type I and Type III hydrogen as well as on molecular nitrogen adsorption further supports the suggestion that these three forms of adsorption occur on or near the same limited pair sites (*27*).

Infrared studies show that the OH and ZnH band frequencies of Type I hydrogen are shifted up and down, respectively, by Type III hydrogen, by oxygen and by nitrogen at −78°K. For oxygen and Type III hydrogen the relative shift in band frequencies is $|10\ \mathrm{cm}^{-1}|$; however, nitrogen effects a larger shift of $|23\ \mathrm{cm}^{-1}|$. This difference is interpreted as being due to the larger steric interaction of nitrogen adsorbed specifically at or near the sites that effect Type I hydrogen adsorption. The shift in frequencies due to oxygen adsorption is seen as a monolayer is approached; however, the shift effected by nitrogen adsorption is seen for a percentage of sites near the initial molecular nitrogen adsorption.

The effect of adsorbed oxygen and nitrogen on the spectrum corresponding to Type III hydrogen is also different (*34*). Both nitrogen and oxygen are more strongly adsorbed than Type III hydrogen. The initial molecular nitrogen adsorption is found to displace Type III hydrogen. The displacement is almost complete when the molecular nitrogen surface coverage is 20%. Oxygen on the other hand does not readily displace Type III hydrogen until a monolayer is approached. The difference in the effect of adsorbed nitrogen and oxygen on the Type I and Type III hydrogen adsorbed on zinc oxide provides a method of distinguishing the role of these two forms of hydrogen in the allotropic conversion and isotopic exchange. The kinetic and adsorption measurements during exchange in the presence and absence of oxygen and nitrogen are compared and their relationship to the various proposed mechanisms are discussed below.

EXPERIMENTAL METHODS

The zinc oxide used in this study was Kadox 25 obtained from the New Jersey Zinc Co. Samples ranging in size from 0.1 to 20 g were pressed at 25,000 psi in a stainless steel plug and were broken up before weighing in order to improve the flow characteristics. As a standard activation procedure, the sample was degassed as the temperature was gradually raised from room temperature to 450°C. Oxygen at a pressure of 170 Torr was then circulated over the catalyst at 450°C for a period of 2 hr. The pressure was maintained by circulating the oxygen through a liquid nitrogen bath at 78°K. If the activity of the catalyst had decreased significantly, oxygen activation was preceded by a 1 hr circulation of hydrogen gas at 450°C, followed by a 2 hr evacuation. Subsequent to the 2 hr oxygen circulation, the catalyst was cooled to room temperature in oxygen. The oxygen was then pumped out for a period of several hours. This procedure was employed because it yields samples with good transmission in the infrared and provides catalysts directly comparable with those used for previously published studies (*24–29*). Surface areas as measured by BET nitrogen adsorption were 8.3 m^2/g for initial activation and, after prolonged use, degenerated to about 6 m^2/g.

Hydrogen and deuterium were purified by slow passage through an activated charcoal trap at 78°K. The nominal purity of the deuterium was 99.5%.

Oxygen and nitrogen (both 99.9% pure) were purified by passage through a trap at 78°K. They were stored in three-liter glass bulbs for use. The quantities adsorbed were measured by a standard BET mercury bulb system.

Analysis of the allotropic concentration of the reacting hydrogen was monitored by two methods. Figure 1 is a schematic representation of the system employed. In both methods reacting and adsorbed gases were introduced from the manifold (1) and measured by the bulb system (2). The first method involved chromatographic separation of small aliquots (less than 1% of the 345 cm^3 reacting volume). Two columns in

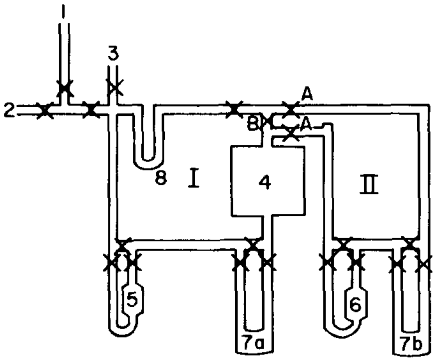

FIG. 1. Circulation system employed for allotropic conversion and isotopic exchange studies (see text). (1) Manifold, sample gases, oil diffusion pump, McLeod and ionization pressure gauges; (2) BET and gas measuring bulbs, and manometer; (3) chromatographic allotropic and isotopic hydrogen analysis (see text) (4) magnetic, glass-enclosed plunger circulation pump; (5) zinc oxide sample; (6) Pt and Cr_2O_3 rapid allotropic conversion catalyst; (7) thermal conductivity bridge; (a) sample arm; (b) reference arm; (8) trap at 78°K. Note: With stopcocks labeled "A" closed system II is bypassed in circulation and with "B" closed and "A" open systems I and II function in tandem.

series at 78°K were employed, a 1.5 m alumina column to separate the allotropes and a 0.5 m column of alumina supported Fe^{3+} to separate the isotopes. The effluent hydrogen was converted to water over a CuO column at 500°C before it passed through the sample arm of the 120°C thermistor bridge.

Improved separation of both the allotropes and isotopes of hydrogen (but not ortho and para deuterium) was achieved by dosing the columns several times with purified carbon dioxide followed by rapid quenching of the columns from room temperature to 78°K immediately following the final CO_2 dose. The columns were activated in flowing helium at 135°C for a period of 6 to 12 hr and were then cooled to room temperature before the CO_2 treatment.

The second method of analysis employed gas phase thermal conductivity measurements to obtain a comparison between the conversion of ortho–para deuterium and ortho-hydrogen at low temperatures. This involved use of systems I and II, in tandem, as shown in Fig. 1. The conductivity difference was measured at 78°K between hydrogen or deuterium (equilibrated at the reacting temperature over pure α-chromia in the reference arm (7b) and bypassed during the run) and the reacting gas in the sample arm (7a). Reproducibility was achieved to within 20% by this method and compared favorably with the results for hydrogen by the previous method. Possible contamination of the filaments by oxygen and nitrogen and the small thermal conductivity changes during a run limited the reproducible application of this method to the comparison of H_2 and D_2 conversion rates at temperatures near 78°K in the absence of adsorbed oxygen or nitrogen.

The temperature of the catalyst was maintained at 78 and 90°K by liquid nitrogen and liquid oxygen baths, respectively. A temperature of 138°K was achieved by a solid–liquid equilibrium bath of 2,3-dimethylpentane.

At temperatures above 138°K a large residual gas phase pressure of oxygen was required to obtain a sufficiently large variation in surface coverage. This gas phase oxygen would catalyze the ortho–para conversion on the alumina column (*33–35*). Therefore, measurements of the conversion in the presence of oxygen were restricted to temperatures below 138°K.

RESULTS

Oxygen promotion of allotropic conversion. The adsorption of oxygen on a surface has been shown to promote the catalysis of ortho–para conversion (*12*). Figure 2 shows the effect of adsorbed oxygen on the ortho–para conversion rate at 78°K. A maximum is seen which approximately corresponds to one half a monolayer of adsorbed oxygen. The experimental first order constant for both allotropic conversion and isotopic exchange as reported

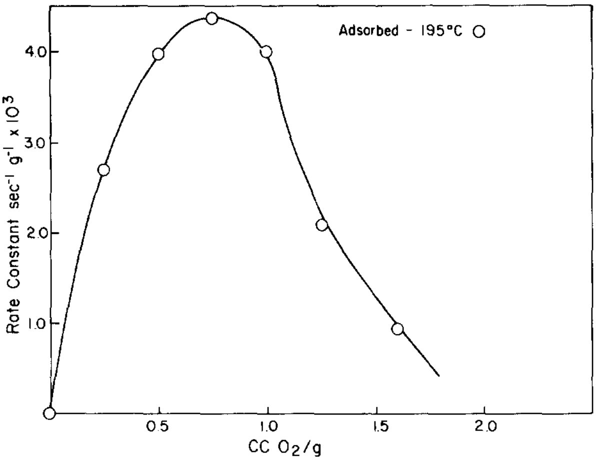

FIG. 2. Allotropic conversion rate as a function of oxygen adsorption on zinc oxide.

below is defined as

$$k(g^{-1}\,s^{-1}) = \frac{1}{gt}\ln\frac{x_o - x_e}{x_t - x_e},$$

where the fraction of para hydrogen, para deuterium or hydrogen deuteride is x_0 at zero time, x_t at time t seconds, and x_e at equilibrium, and g is the catalyst size in grams. If n is the number of hydrogen molecules in the circulation system and A is the area of the zinc oxide catalyst, the absolute rate constant as defined by Acres, Eley and Trillo (*35*) is k_m (molecules cm^{-2} s^{-1}) and the two constants are related by

$$k_m = nkg/A.$$

This last factor is approximately equal to $k \times 3 \times 10^{16}$ (molecules cm^{-2} s^{-1}) and corresponds to the freshly activated catalyst (with a typical area of 8 m^2 g^{-1}), the reaction volume and pressure employed in the ortho–para hydrogen conversion and isotopic equilibrium runs, but as the surface area decreased, as was the case for H_2–D_2 exchange on subsequent activations (to about 6 m^2 g^{-1}), this factor would increase accordingly. This is the case for the comparison of hydrogen vs deuterium ortho–para conversion to the other rates. It is given for rapid approximate comparison to other rate data.

Nitrogen inhibition of allotropic conversion. The effect on the rate of conversion by nitrogen adsorbed on a catalyst for which the rate was promoted by adsorption of 0.25 cm^3 g^{-1} of oxygen at 78°K is shown in Fig. 3. The circles and squares represent different runs. The triangle represents addition of 0.5 cm^3 g^{-1} of oxygen to the sample after addition of 0.5 cm^3 g^{-1} N_2 to the promoted catalyst. The darkened circles correspond to runs for which the adsorbed gases were added at room temperature and the catalyst was quenched from room temperature to the reaction temperature to achieve the noted adsorption. Similar plots were achieved for nitrogen adsorption on catalysts promoted by 0.05 and 0.125 cm^{-3} O_2. The initial slope of these poisoning experiments extrapolate to complete poisoning at around 0.3 cm^3 g^{-1} coverage. This corresponds to 15% surface coverage by nitrogen. Nitrogen also inhibits the ortho–para conversion in the absence of oxygen promotion. However, the reactions become too slow to determine reliable rates.

Effect of nitrogen and oxygen on isotherms for reversibly adsorbed hydrogen. The adsorption of reversibly adsorbed hydrogen after presorption of irreversible hydrogen on zinc oxide at 78°K is shown in Fig. 4. Hydrogen was presorbed at room temperature and cooled to 78°K in

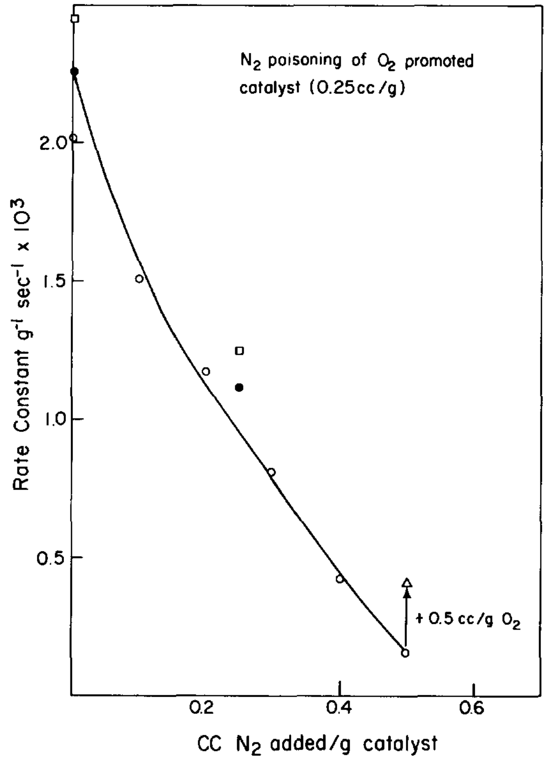

FIG. 3. Poisoning of allotropic conversion rate by nitrogen for a catalyst that had been promoted by oxygen. O ≡ 10^{-6} g^{-1} s^{-1}.

hydrogen. The reversible hydrogen was evacuated and adsorption measurements were performed as a function of pressure as well as presorbed oxygen and/or nitrogen as indicated.

Comparison of nitrogen and oxygen effects for allotropic conversion and isotopic exchange. The rates of ortho–para hydrogen conversion and hydrogen–deuterium exchange were measured at 138°K

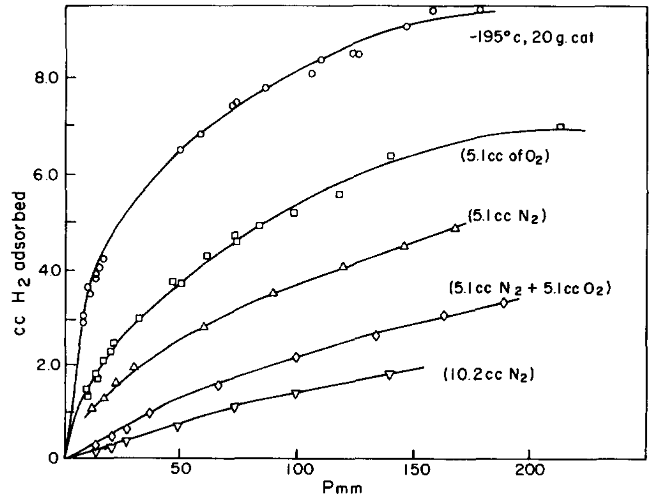

FIG. 4. Adsorption of reversible hydrogen at 78°K as a function of pressure in the presence of presorbed nitrogen and oxygen.

TABLE 1
RATES OF ORTHO-PARA CONVERSION AND ISOTOPIC HYDROGEN EXCHANGE AT 138°K

Run No.	Reactant mixture (Torr)	$k_{o-p}(\times 10^4\ g^{-1}\ s^{-1})$	$k_{H_2-D_2}(\times 10^6\ g^{-1}\ s^{-1})$
1	200 hydrogen	1.65	1.0
2	200 hydrogen and 100 N_2	0.095	0.7
3	200 hydrogen	1.5	0.8
4	200 hydrogen and 100 N_2	0.10	0.8
5	200 hydrogen and 30 O_2	120	0.8
6	200 hydrogen	0.85	0.7

where the exchange rates could be measured and sufficient nitrogen and oxygen could be adsorbed to achieve promotion and poisoning of the para-conversion rate where the indicated amount of nitrogen or oxygen and 200 Torr of H_2 (about 100 cc) were premixed. The nitrogen or oxygen was partially adsorbed though the extent of adsorption was not measured. The results are listed in Table 1.

Ethylene inhibition of allotropic conversion. The rate of ortho-para conversion at room temperature was measured for a 200 Torr hydrogen pressure in the presence of 100 Torr ethylene in the gas phase. The rate decreased from $2.3 \times 10^{-2}\ g^{-1}\ s^{-1}$ without ethylene, to $0.8 \times 10^{-2}\ g^{-1}\ s^{-1}$ with ethylene. Previously published data under similar conditions for the effect of 100 Torr ethylene on the hydrogen-deuterium exchange rate indicates a rate without ethylene of $3.2 \times 10^{-3}\ g^{-1}\ s^{-1}$ compared to a rate of $1.1 \times 10^{-3}\ g^{-1}\ s^{-1}$ in the presence of ethylene for a system with a volume of 228 cm^3 (*29*).

Kinetic isotope effect in allotropic conversion. The second method of analysis was used to obtain the rates of ortho-para conversion for deuterium and hydrogen. The results at 78°K were for deuterium, $k = 2 \times 10^{-6}\ g^{-1}\ s^{-1}$, and for hydrogen $k = 0.7 \times 10^{-6}\ g^{-1}\ s^{-1}$. The rate of deuterium conversion is slightly greater than the rate of hydrogen conversion. With the conversion promoted by oxygen at 78°K a normal isotope effect (*12*) is found with the rate of hydrogen conversion greater than the rate of conversion for deuterium.

DISCUSSION

Possible mechanism for allotropic conversion and exchange. Three basic mechanisms have been proposed for allotropic conversion on the surface of a catalyst. With a zinc oxide catalyst, the active site has been proposed as an isolated zinc oxide pair that is capable of the dissociative adsorption (Type I) of hydrogen (giving rise to bands that correspond to ZnH and OH bonds) as well as adsorption at low temperature of a molecular species of hydrogen (Type III) at or near such pair sites. These mechanisms for Types I and III hydrogen can be schematically represented for a zinc oxide surface (Fig. 5). H and H′ are hydrogen or deuterium atoms and the primes are employed throughout each individual mechanism to indicate whether there is either exchange between atomic hydrogen from nearby sites, as in (A), or exchange between molecular and atomic hydrogen, as in (B) and (C).

Some relevant comments and observations are appropriate on each of these proposed mechanisms:

A. 1. Proposed by Bonhoeffer and Farkas (*5*).

2. Conversion will be faster than exchange if $k_{-1A} \gg k_{2A} + k'_{2A}$ or will be equal if $k_{1A} \ll k_{2A} + k'_{2A}$ and the surface site to site exchange occurs rapidly.

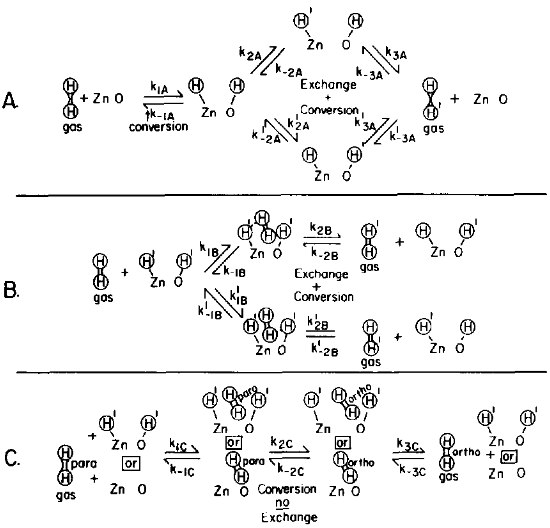

FIG. 5. Possible mechanisms for exchange and conversion on zinc oxide.

3. Surface mobility of hydrogen bound to zinc or oxygen atoms of the pair site is necessary for exchange.

4. Molecular hydrogen adsorbed on the pair site would hinder the reaction if it had any effect at all.

B. 1. Proposed by Rideal (*6*) and Eley (*4*).

2. The rates of conversion and exchange will always be the same order of magnitude, neglecting isotope effects, and exchange with adsorbed Type I hydrogen is implied.

3. Molecular hydrogen is an intermediate and the degree of surface coverage could have direct effect on the rate of conversion.

C. 1. Proposed by Farkas *et al.* (*10–13*) and with modifications by Van Cauwelaert and Hall (*16*).

2. No exchange implied or necessary for conversion as in A or B.

3. Molecular hydrogen would be the intermediate and, therefore, the rate of conversion would be directly related to the surface coverage by Type III hydrogen.

Mechanisms for allotropic conversion at low temperature. Data given in the introduction indicate that Type III hydrogen, oxygen, and nitrogen are all adsorbed in the vicinity of Type I hydrogen and that nitrogen and oxygen both can replace Type III hydrogen, although nitrogen is bound more specifically than is oxygen to sites adjacent to Type I hydrogen. These conclusions are in complete agreement with the isotherms presented in Fig. 4.

Hydrogen adsorption without O_2 or N_2 is shown in the upper curve. The shape of the curve indicates a rapid chemical adsorption followed by "linear" physical adsorption, where the term linear applies to the dependence on pressure, implying a lower heat of adsorption. Adsorption of 5.1 cm^3 of oxygen yields reversible hydrogen adsorption characteristic of the same type as was seen in the absence of oxygen for a catalyst of correspondingly lower surface. Nitrogen adsorption, on the other hand, significantly decreases the amount of nonlinear adsorption. Not only does it effect a correspondingly greater decrease than for oxygen, but the nature of the adsorption resembles linear physical adsorption. These results may be interpreted as selective blocking of the Type III molecular chemical adsorption by nitrogen and not by oxygen, and blockage of overall hydrogen adsorption in a random fashion by both.

There are striking parallels between the results of ir and adsorption studies on Type III hydrogen and the results of kinetic studies on the effect of oxygen and nitrogen on allotropic conversion at low temperatures. Figure 3 shows that nitrogen reverses the promotional effect of oxygen on conversion. Extrapolation of the initial slope of this curve indicates that complete poisoning would occur at a nitrogen coverage of 10 to 20% in agreement with the replacement of Type III hydrogen as indicated by ir spectra at a 10% surface coverage of N_2. Furthermore, the fact that readdition of oxygen does not restore activity is in agreement with the results mentioned in the introduction that oxygen is effective in completely displacing Type III hydrogen only at almost monolayer coverage, implying random adsorption of oxygen. These similarities suggest that Type III hydrogen may indeed be an intermediate in ortho–para conversion.

If Type III hydrogen is an important intermediate, the promotion of allotropic conversion by O_2 would probably be caused by oxygen being adsorbed near a Type III hydrogen. If, as is implied by the data already presented, oxygen is adsorbed randomly, then for an oxygen surface coverage of θ_o, we would expect the number of Type III sites which could be covered by hydrogen to be $N_s(1-\theta_0)$, where N_s is the total number of Type III sites. The rate of allotropic conversion should then be proportional to the number of Type III hydrogens adjacent to adsorbed oxygen and, therefore, we would expect

$$R = k\,N_s(1-\theta_0)\theta_o. \qquad (1)$$

Such a rate law would yield a maximum at half monolayer coverage in qualitative agreement with Fig. 2.

The close similarity between allotropic conversion and Type III hydrogen makes mechanism A highly unlikely. In addition the inverse kinetic isotope effect for ortho–para conversion would not be expected for mechanism A if the allotropic conversion rate were very fast in comparison to the isotopic exchange rate. Table 1 shows that conversion is indeed much more rapid than exchange. Since mechanism B requires the two rates to be comparable, and not independent as shown in Table 1, it too is excluded; we therefore conclude that the allotropic conversion must take place by the *molecular* mechanism C.

Mechanism for isotopic exchange. Both mechanisms A and B would result in exchange over zinc oxide. It has been suggested that mechanism B is dominant for exchange near room temperature. However, the equilibrium isotopic ratio ($H_a^2/H_2 : D_a^2/D_2$) based on this mechanism can be calculated from the published rate constants[2] and is found to be 142 at 213°K. This value seems unreasonable. The reported rate constants were calculated assuming no kinetic isotope effect on adsorption. However, the adsorption of HD on zinc oxide below room temperature indicates a marked kinetic isotope effect but no significant equilibrium isotope effect (*28*) on adsorption. Mechanism B is not necessarily dominant.

Comparison of the conversion and exchange rates given in Table 1 shows that the two processes involve different mechanisms at low temperature. Unlike the conversion rate the exchange rate does not reflect the behavior of Type III hydrogen. Consequently, mechanism B involving Type III hydrogen is eliminated. Since it

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[2] Tabulated rate constants (*36*) give rise to the following equilibrium calculation:

$$K_{E_1} = \frac{(\mathrm{HD})(\mathrm{H_a})}{(\mathrm{D_a})(\mathrm{H_2})} = \frac{1.2\times10^{-4}}{1.1\times10^{-5}} = 10.9$$

and

$$K_{E_2} = \frac{(\mathrm{HD})(\mathrm{D_a})}{(\mathrm{H_a})(\mathrm{D_2})} = \frac{1.0\times10^{-5}}{1.3\times10^{-4}} = 0.0777,$$

$$\frac{K_{E_1}}{K_{E_2}} = \frac{(\mathrm{H_a})^2(\mathrm{D_2})}{(\mathrm{H_2})(\mathrm{D_a})^2} = \frac{\mathrm{H_a}^2/\mathrm{H_2}}{\mathrm{D_a}^2/\mathrm{D_2}} = 142.$$

seems unlikely that a Rideal–Eley mechanism, B, is effected via the most weakly bound form of molecular hydrogen, we regard some form of the Bonhoeffer–Farkas mechanism, A, as the likely pathway for the low temperature exchange.

The ratio of the allotropic conversion rate in the absence of ethylene to the rate in the presence of ethylene reported in this paper is 2.9 at room temperature. The same numerical ratio was obtained for the isotopic exchange rate in the absence and presence of ethylene under similar conditions (*29*). This result may be indicative of a similar mechanism for the two reactions at room temperature, or may indicate a similar surface intermediate for the reaction. However, the allotropic conversion rate is an order of magnitude greater than the exchange rate. Mechanism B would predict the same order of magnitude for the two rates. Mechanism A is probably dominant at room temperature.

The simplest interpretation of our data is that the exchange reaction occurs by mechanism A at all temperatures.

Comparison of H_2 and D_2 allotropic conversion. We have concluded that the ortho–para conversion at low temperature occurs by mechanism C. The following discussion shows that the observed difference between the rate for hydrogen and for deuterium in the absence of oxygen is consistent with this mechanism and also explains the difference between rates in the gas phase and on the ZnO surface.

Adsorbed hindered rotor and the paramagnetic conversion. The allotropic conversion by a paramagnetic mechanism has been treated theoretically for gas phase molecular collision with a paramagnetic molecule by Wigner (*8*). As noted by Van Cauwelaert and Hall (*16*), the collision probability W_{01} can be properly defined by

$$W_{01} = \frac{\langle \psi_o | \mathcal{H}' | \psi_p \rangle^2}{(E_o - E_p)^2}, \qquad (2)$$

where ψ_o and ψ_p are the wave functions for ortho and para, respectively, $\mathcal{H}'$ is the paramagnetic perturbation and E_o represents the energy of the ortho states and E_p the energy of the para states. More specifically, the transition can be written for hydrogen as

$$W_{01} = \frac{36\mu_a^2\mu_p^2a^2}{\hbar^2 r^8 \omega^2} \sin^2 \frac{\omega t}{2} \langle \cos\theta \rangle^2, \qquad (3)$$

where

μ_a	magnetic moment of perturbing paramagnetic site
μ_p	magnetic moment of the proton
a	hydrogen internuclear distance
$\hbar$	Planck's constant divided by 2π
r	distance of approach of center of mass of hydrogen molecule to the site
t	time at distance of approach r
$\langle \cos\theta \rangle$	average value of cosine of angle between **r** and **a**
ω	$(E_1 - E_o)/\hbar$

This can be generalized as

$$W_{01} = \frac{C}{\omega^2} \sin^2 \left(\frac{\omega t}{2}\right) \langle \cos\theta \rangle^2. \qquad (4)$$

For a collision with a paramagnetic site $\omega t/2 \ll 1$, the sine squared of an argument is replaced by the argument squared and $\langle \cos\theta \rangle^2$ is calculated as 1/3 for $J = 0 \rightarrow J = 1$, a substitution employed by Wigner. This results in the classic equation (*8*) as follows,

$$W_{01} = \frac{3\mu_a^2\mu_p^2a^2t^2}{\hbar^2 r^8}. \qquad (5)$$

At longer times (i.e., for an adsorbed molecule) where $\omega t/2 \gg 1$ the average transition can be evaluated for a surface residence probability at time t of $P(t)$. If k is the kinetic desorption rate constant such that $dP(t)/dt = -kP(t)$, the transition probability (4) can be integrated with respect to $dP(t)$ ($\equiv -ke^{-kt}dt$). The resulting equation reflects the average transition probability of an atom adsorbed on the surface

$\left[=\int_0^\infty W_{01}dP(t)\right]$. With appropriate normalization the equation can be written

$$\langle \overline{W}_{01}\rangle = \frac{C}{\omega^2}\frac{(\omega/k)^2}{1+(\omega/k)^2}\langle\cos\theta\rangle^2, \quad (6)$$

as ω/k becomes much less than 1, Eq. (6) becomes

$$\langle \overline{W}_{01}\rangle = \frac{C}{k^2}\langle\cos\theta\rangle^2. \quad (7)$$

This is the approximation for a collision interaction and, therefore, the effective adsorption and desorption rates are equal and $1/k$ can be replaced by $\tau/2$ where τ is the average total time of interaction. Therefore, Eq. (7) becomes

$$\langle \overline{W}_{01}\rangle = \frac{C\tau^2}{4}\langle\cos\theta\rangle^2. \quad (8)$$

This is identical to Eq. (5). As the residence time becomes large, ω/k becomes greater than 1 and Eq. (6) becomes

$$\langle \overline{W}_{01}\rangle = \frac{C}{\omega^2}\langle\cos\theta\rangle^2. \quad (9)$$

For an endothermic reaction at low temperatures (where only the $J = 0$ to $J = 1$ transition is to be considered) the rate of transition on the surface can be written for N_s adsorbed molecules in $J = 0$ as

$$R_{01} = \frac{N_s}{\tau}\langle W_{01}\rangle\, e^{-\Delta E/kt}. \quad (10)$$

For zinc oxide (*25,27,28*) a sizeable barrier to rotation is needed to account for the measured isotope effect [$(D_{2a}/H_{2a})_\theta$] of 1.57; furthermore, the failure to observe $\Delta J = 2$ bands in the infrared (indicating that their intensity is an order of magnitude less than the observed $\Delta J = 0$ bands) also suggests a high barrier to rotation. The observation of infrared bands corresponding to molecular hydrogen, which are forbidden in the gas phase, is a result of this hindered rotation and its effect on the induced dipole moment of the adsorbed molecular species. The difference in the perpendicular and parallel component of the polarizability of the adsorbed hydrogen molecule (0.21 Å^3) allows chromatographic separation of the allotropes (*15*). Hindered rotation of a surface adsorbed molecule also changes the energy levels of the adsorbed molecule. If such an effect takes place, the ratio of the rate with different E level spacing (R_{01}) to the rate with the same E level spacing ($R_{01}{}^0$) (as is the case in the gas phase) is

$$\frac{R_{01}}{R_{01}{}^0} = \frac{\langle W_{01}\rangle}{\langle W_{01}\rangle^0}\, e^{-(\Delta E-\Delta E)/kt}$$
$$= \frac{\langle\cos\theta\rangle^2}{\langle\cos\theta\rangle^{02}}\left(\frac{\omega_0}{\omega}\right)^2 e^{-(\Delta E-\Delta E)/kt}. \quad (11)$$

King and Benson (15) have provided a graphic estimation of the effect on these energy levels by the barrier height to rotation. For a barrier to rotation of 2 kcal at 78°K $(R_{01}/R_{01}{}^0)_{H_2} = 263$ [$\langle\cos\theta\rangle^2/\langle\cos\theta\rangle^{02} = 789$ as the ratio of the cosine terms is on the order of three due to the preferred orientation of the hydrogen perpendicular to the surface (*15*). For deuterium the effect is even more dramatic where it can be estimated that for the same barrier to rotation at 78°K

$$\left(\frac{R_{01}}{R_{01}{}^0}\right)_{D_2} = \frac{\langle\cos\theta\rangle^2}{\langle\cos\theta\rangle^{02}}\, 9.6\times 10^3 = 2.9\times 10^4.$$

This explains the change in the ratio of the rates of ortho–para conversion of hydrogen to deuterium which is 5.4:1 in the gas phase at 83°K to a ratio of about 1:2 on the surface of zinc oxide at 78°K. The hindering of rotation effects a change in energy level differences that is more dramatic for deuterium than for hydrogen and, therefore, the rate of conversion for deuterium can be greater than that for hydrogen.

CONCLUSION

For zinc oxide it is therefore concluded that isotopic exchange of hydrogen at room temperature and below occurs by some form of the Bonhoeffer–Farkas mechanism, involving Type I hydrogen, while allotropic conversion of hydrogen is dominated at low temperatures by a paramagnetic conversion of a molecular adsorbed hydrogen species. This mechanism is enhanced by the high barrier to rotation for Type III molecular hydrogen. At room temperature where Type III hydrogen is not evident, the allotropic conversion is dominated by an adsorption–desorption mechanism involving atomic hydrogen where the slower site-to-site exchange makes the conversion proceed more rapidly than the H_2–D_2 exchange. One effect of the high barrier to rotation over zinc oxide is to increase the low temperature allotropic conversion of deuterium to a greater extent than hydrogen.

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