

**Nature of Urea–Water Interactions.** Although urea causes a breakdown of long-range order, the water in concentrated urea solutions is nevertheless extensively hydrogen bonded, as evidenced by the fact that  $\delta_w$  is still strongly temperature dependent (the increase in “structural temperature” is only moderate). That this hydrogen bonding involves the urea molecules is suggested by the upfield shift of  $\delta_u$  with increasing temperature. The high solubility of urea suggests the existence of some urea–water interactions. Other studies<sup>31</sup> have shown that  $\delta_w$  contains an appreciable downfield contribution due to urea–water interactions. However, ultrasound attenuation results<sup>33</sup> indicate that there are no extended structures involving urea and water, and the existence of two easily resolvable dielectric relaxations in 8 M urea<sup>37</sup> shows that urea and water molecules tumble independently. Urea–water association is therefore short-range and short-lived. Such association slightly retards the tumbling of the urea molecules, as may be seen by comparison of our  $\tau_c$  results with those<sup>40</sup> for mixtures of water with acetone, which is isoelectronic with and of similar shape to urea. The  $\tau_c$  of acetone remains roughly constant, *ca.*  $1 \times 10^{-12}$  sec over the whole composition range, while that of the water shows a maximum at about 30 mol % acetone. The latter observation is ascribed to a water structuring process for which there is no evidence in the urea–water mixtures. The linear nature of the Arrhenius plots for the urea  $\tau_c$  and the values of the activation energies confirm that the tumbling species is not a urea–water complex. The fact that the proton exchange rate is

(40) E. v. Goldammer and M. D. Zeidler, *Ber. Bunsenges. Phys. Chem.*, **73**, 4 (1969).

slow also indicates that urea–water hydrogen bonding is only short-lived (*cf.* a rate of *ca.*  $10^3$  sec<sup>-1</sup> for water–water proton exchange in pure water). This agrees with observations that in water the presence of structure-breaking ions slows down the exchange rate.<sup>41</sup>

## Conclusions

We can draw the following conclusions about the structures and interactions in a concentrated urea solution. (i) The long-range order characteristic of pure water is destroyed and is not replaced by extended structures involving urea molecules. (ii) There are no urea dimers or higher polymers. (iii) There are extensive short-range, short-lived interactions between water and urea, involving hydrogen bonds to the urea  $\text{NH}_2$ 's and possibly to the urea  $\text{C}=\text{O}$ .

These conclusions fit the model<sup>13</sup> which proposes that urea displaces the water equilibrium from a bulky species involving long-range order to a dense species involving only short-range structure, by resembling water in its capability to form hydrogen bonds but by having the wrong geometry to take part in extended water structures. The resemblance to water explains the high solubility of urea.

**Acknowledgments.** We are grateful to Dr. R. Pottel for communicating dielectric relaxation results in advance of publication and to Dr. G. J. T. Tiddy for performing the <sup>14</sup>N relaxation measurements. We are pleased to acknowledge the technical assistance for Mr. S. Ablett and Mr. G. Wit.

(41) H. G. Hertz and R. Klute, *Z. Phys. Chem.*, **69**, 101 (1907).

## Infrared Studies of Isotope Effects for Hydrogen Adsorption on Zinc Oxide

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**Abstract:** Kinetic and equilibrium isotope effects were studied for type I hydrogen, deuterium, and hydrogen deuteride adsorption on zinc oxide. At room temperature, there is no equilibrium isotope effect for hydrogen *vs.* deuterium, but the preferred form of adsorption of hydrogen deuteride appears to be  $\text{ZnH-OD}$  rather than  $\text{ZnD-OH}$  by a factor of 2–3. Kinetic isotope measurements reveal that hydrogen adsorbs faster than deuterium by a factor of at least 5 at  $-195^\circ$ . The kinetic isotope effect for HD at  $-195^\circ$  reveals  $\text{ZnD-OH}$  is the favored form by a factor of 20–100. Approximate computations of these effects based on observed ir frequencies reveal that these effects are explicable provided we assume the bending vibrations for adsorbed species are either very low frequency compared to those observed for simple molecules or that the adsorption is mobile at room temperature.

Hydrogen chemisorption on zinc oxide at or above room temperature occurs in two stages: the first stage is characteristically rapid and is complete in a few minutes; the second stage is characteristically slow and continues for at least 24 hr.<sup>2–4</sup> The nature of these ad-

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(2) H. S. Taylor and D. V. Sickman, *J. Amer. Chem. Soc.*, **54**, 602 (1932); H. S. Taylor and C. O. Strother, *ibid.*, **56**, 586 (1934); V. Kesavulu and H. A. Taylor, *J. Phys. Chem.*, **64**, 1124 (1960).

sorbed species has been the subject of many discussions.<sup>2–8</sup> Pace and Taylor, in a classic paper,<sup>5</sup> examined

- (3) G. Parravano and M. Boudart, *Advan. Catal.*, **7**, 47 (1955).
- (4) A. L. Dent and R. J. Kokes, *J. Phys. Chem.*, **73**, 3772 (1969).
- (5) J. Pace and H. S. Taylor, *J. Chem. Phys.*, **2**, 578 (1934).
- (6) M. Boudart and H. Taylor, L. Farkas Memorial Volume, *Res. Coun. Isr.*, **223** (1952); G. Parravano, H. G. Friedrich, and M. Boudart, *J. Phys. Chem.*, **63**, 1144 (1959).
- (7) R. P. Eischens, W. A. Pliskin, and M. J. D. Low, *J. Catal.*, **1**, 180 (1962).
- (8) For a different viewpoint, see D. Naragana, V. S. Subrahmanyam

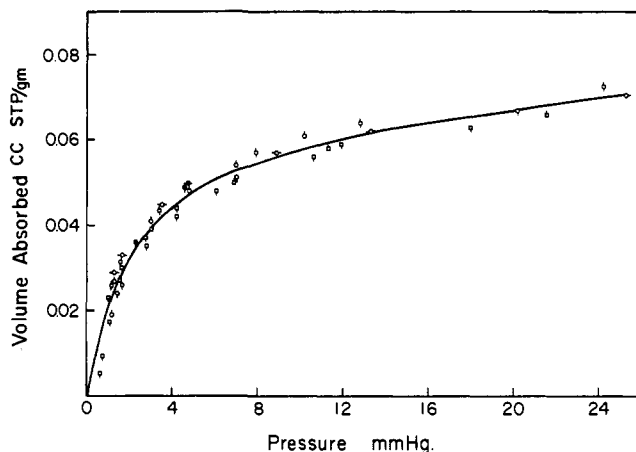


Figure 1. Type I hydrogen isotherms: (○) run 1, H<sub>2</sub>; (□) run 2, D<sub>2</sub>; (△) run 3, H<sub>2</sub>; (◇) run 4, D<sub>2</sub>; (◊) run 5, H<sub>2</sub>; (●) run 6, H<sub>2</sub>. Solid points are desorption points.

kinetic isotope effects for slow hydrogen adsorption on related systems. Some time later these studies were extended to zinc oxide.<sup>6</sup> Both of these studies led to the conclusion that the slow hydrogen adsorption (for which no isotope effect was observed) involved a rate-determining step characteristic of the solid only. More recently, Eischens, Pliskin, and Low<sup>7</sup> carried out an infrared study of chemisorbed hydrogen which revealed that hydrogen chemisorbed on zinc oxide yielded bands characteristic of Zn-H and O-H species. Then, Dent and Kokes<sup>4</sup> provided an experimental basis for a consistent operational definition for two types of hydrogen adsorption on zinc oxide at room temperature. Type I hydrogen adsorption was found to be reversible and all of this occurred rapidly; type II hydrogen adsorption was found to be irreversible and some of this occurred rapidly and some of it occurred slowly. It was further found that only the type I chemisorption yields the ir bands characteristic of ZnH and OH species and that only the type I chemisorption was effective in ethylene hydrogenation. Recently, Tamaru and coworkers<sup>9,10</sup> have provided support for this picture of hydrogen adsorption.

These developments suggested that a study of isotope effects for type I hydrogen adsorption might be informative. Type I hydrogen can be separated from type II hydrogen if the surface is first saturated with the latter. At room temperature type I adsorption is reversible and equilibrium data are obtainable; at low temperatures, *e.g.*, below  $-40^{\circ}$ , the adsorption is irreversible and the amount of adsorption is kinetically controlled.<sup>9</sup> Thus, both equilibrium and kinetic isotope effects can be studied. The magnitude of these effects is determined by the vibrational partition functions for the adsorbed species and activated complex. We have at least partial experimental data on the vibrational spectrum of this adsorbed hydrogen, which is required for evaluation of the partition function; hence, it was felt that a reasonably complete study of kinetic and thermodynamic isotope effects might be carried out.

J. Lal, M. Mahmoulali, and V. Kesavulu, *J. Phys. Chem.*, **74**, 779 (1970); and D. Naragana, J. Lal, and V. Kesavulu, *ibid.*, **74**, 4150 (1970).

(9) S. Naito, H. Shimizu, E. Hagiwara, T. Onishi, and K. Tamaru, *Trans. Faraday Soc.*, **67**, 1519 (1971).

(10) S. Naito, Y. Sakurai, H. Shimizu, T. Onishi, and K. Tamaru, *ibid.*, **67**, 1529 (1971).

In this paper we report the results of such a study of the adsorption on zinc oxide of hydrogen, deuterium, and hydrogen deuteride.

## Experimental Section

**Materials.** All samples of zinc oxide were Kadox-25 of the N. J. Zinc Co.

Tank hydrogen and deuterium were purified by passage through a charcoal trap at  $-195^{\circ}$ . The nominal isotopic purity of the deuterium was 99.5%. HD was obtained from the International Chemical and Nuclear Corp. in Irvine, Calif., and was purified by passage through an empty trap at  $-195^{\circ}$ . Mass spectroscopic analysis indicated that the isotopic impurities were 1.2% D<sub>2</sub> and 3.8% H<sub>2</sub>. This composition remained essentially unchanged even after 1 year of storage in a glass bulb.

**Adsorption Studies.** All adsorption studies including those in ir cells were carried out with the standard oxygen pretreatment described earlier.<sup>4,11</sup> Adsorption isotherms were determined on a 23.0-g sample. In these runs the type I hydrogen (deuterium) was measured after saturation with type II hydrogen (deuterium) by overnight adsorption followed by a 30-min evacuation at room temperature. It was assumed equilibrium was reached when the increase in adsorption with time was less than 0.001 cc/g in 15 min. On this basis adsorption equilibrium was over 90% complete in 30 min and equilibrium was reached within 1 hr. Desorption points, obtained by decreasing the pressure, took somewhat longer to reach equilibrium.

**Infrared Studies.** The sample cell for these studies consisted of an 8-cm stainless steel tube 2.3 cm in diameter with cooling jackets at the end to which NaCl windows were attached. The central part had a wall thickness of about 0.050 in. and was wrapped with a nichrome heating wire and jacketed so that it could be surrounded by a refrigerating bath. The two ends of the tube (each about 2 cm) were turned down to about 0.008-in. wall thickness to minimize heat conduction to or from the windows. The catalyst sample was positioned in the central portion of the tube and its temperature was monitored by a thermocouple junction in contact with the sample disk about 5 mm from the edge. With liquid nitrogen as a coolant the thermocouple gave readings corresponding to  $-195^{\circ}$ . All temperatures reported herein are the thermocouple readings. With the infrared beam passing through the sample it is likely that some heating occurred at the center of the disk; hence, the reported temperatures should be viewed as approximate.

Amounts of observed species should be proportional to the integral of optical density with respect to wavelength. In these studies we approximated this quantity by the product of peak optical density and band half-width. Spot checks revealed that this procedure yielded results comparable to those obtained by point-by-point integration. In a few cases the bands of interest appeared to consist of a slightly separated strong and weak component (see Results). Generally, only the wings of the stronger band were affected by the weaker band whereas the minor band was quite distorted by the stronger band. Since the contribution of the minor band to the overall intensity was small and uncertain, only the parameters of the major band were used to compute the integrated intensity. Reproducibility was reasonably good. For example, five runs made on one sample with regeneration between runs yielded intensities for equilibrated H<sub>2</sub>:D<sub>2</sub> and HD at room temperature ranged from 10.8 to 12.8 cm<sup>-1</sup>. A different sample under somewhat different conditions yielded values ranging from 10.3 to 13.9 cm<sup>-1</sup>. Normalization of the spectrum to the same total intensity further improved the agreement since it minimized uncontrollable variations from one regeneration to another.

The absorption coefficient for a species in the infrared changes on isotopic substitution.<sup>12</sup> Thus, to make comparisons based on amounts, we must know the relative absorption coefficients. To do so, two assumptions were made. First, it was assumed that the amount of ZnH and OH species formed from hydrogen was the same. Second, it was assumed that at saturation the amount of type I hydrogen was equal to the amount of type I deuterium. For two different sequences of experiments carried out under slightly different conditions, this yielded relative absorption coefficients for ZnH, OH, ZnD, OD of 1.00, 0.51, 0.61, 0.43 and 1.00, 0.74, 0.58, 0.50. The difference is greatest for the OH band; this is, in part,

(11) A. L. Dent and R. J. Kokes, *J. Amer. Chem. Soc.*, **92**, 6709 (1970).

(12) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York, N. Y., 1955, p 192.

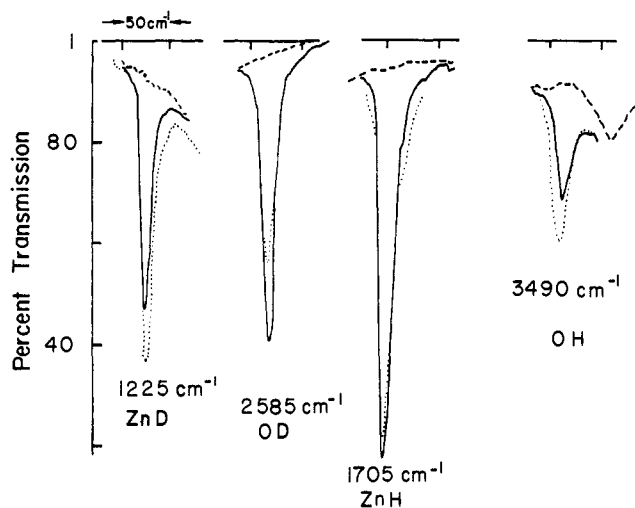


Figure 2. Adsorption of hydrogen and/or deuterium on zinc oxide. The dashed curve is background. The dotted curve is with  $H_2$  or  $D_2$  at 35 mm of pressure. The solid curve is for HD at 70 mm of pressure about 5 min after exposure to the catalyst.

due to the fact that the OH band is superimposed on residual hydroxyl bands of the zinc oxide. In the two sequences of experiments correction for this background was handled differently. Since each sequence had a different calibration run, this difference should cancel; hence, the accuracy is somewhat greater than one would judge from the quoted OH absorption coefficients. Nevertheless, the uncertainty in quantitative comparisons is greatest for the OH band and this uncertainty is greatest when the band intensity is weakest and corrections for background hydroxyls are most critical. For the other bands the uncertainty in quoted values is probably about 10%.

Unless otherwise noted, spectra shown with solid lines are those recorded in the presence of adsorbed hydrogen; spectra shown with broken lines represent the "background" in the absence of adsorbed hydrogen. The spectra were recorded with a Perkin-Elmer 521 grating double-beam spectrometer with a spectral slit width varying from 5 (at  $3600\text{ cm}^{-1}$ ) to  $2\text{ cm}^{-1}$  (at  $1200\text{ cm}^{-1}$ ). Band positions are reported to the nearest  $1\text{ cm}^{-1}$ ; the precision of the measurements was about  $\pm 3\text{ cm}^{-1}$ .

## Results

**Thermodynamic Isotope Effects.** Figure 1 shows hydrogen and deuterium isotherms for type I adsorption (as defined operationally in the Experimental Section). Prior to each run, except run 6, the catalyst was freshly activated. Run 6 was performed by repeating the procedure for saturation with type II hydrogen after completion of run 5. Saturation of the surface occurs above about 40 mm;<sup>4</sup> since isotope effects would not be as evident near saturation, a special effort was made to obtain data well below pressures where saturation effects are dominant. The agreement between adsorption (open symbols) and desorption (solid symbols) shows that even in this low-pressure region, isotherms are reversible as required for true equilibrium.

Comparison of replicate runs shows that if sintering or deactivation took place, its effect was small inasmuch as the scatter of points on either side of the curve was about  $\pm 5\%$  above  $P = 5\text{ mm}$ . Much of this scatter was inherent in the procedure adopted for separation of type II and type I adsorption. If one compares the curves for the initial uptake *vs.* time following each activation, all of the curves for hydrogen were identical within the assumed experimental error in measurement, *i.e.*,  $\pm 0.001\text{ cc/g}$ .

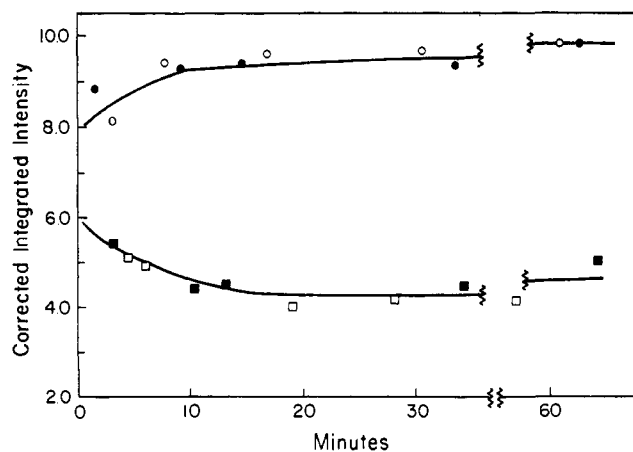
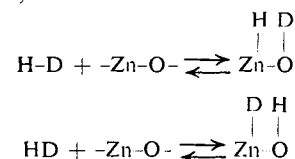


Figure 3. Changes in the adsorbed species with time after exposure to HD at 70 mm. The ordinate is the integrated intensity divided by the absorption coefficient relative to that for ZnH; hence, it corresponds to amounts in arbitrary units: (○) OD; (●) ZnH; (□) OH; (■) ZnH.

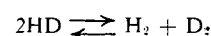
Examination of these data suggests that there is little isotope effect for hydrogen *vs.* deuterium. There is a trend for hydrogen isotherms to be higher than deuterium isotherms, but this trend appears to be comparable to the scatter in the data. Thus, if we plot separate curves for hydrogen and deuterium, the average value for hydrogen adsorption at 10 mm is  $0.058 \pm 0.002$ , whereas that for deuterium is  $0.056 \pm 0.001\text{ cc/g}$ . Data obtained from infrared intensities are less accurate than those for the isotherms. Nevertheless, results of infrared studies support the adsorption studies inasmuch as intensity data suggest that the amount of hydrogen adsorption at a given pressure is about the same as the amount of deuterium adsorption at that pressure.

The dotted curves in Figure 2 show the room temperature spectra of hydrogen at a pressure of 35 mm and deuterium at a pressure of 35 mm. On this same plot indicated by a solid line is a corresponding spectrum for HD at a pressure of 70 mm taken 5-10 min after exposure to HD. Saturation effects are pronounced at these pressures; hence, the sums of corrected intensities for the separate spectra for hydrogen and deuterium should not yield the same intensity sum found for HD at the higher pressures. The remarkable feature of these spectra is the fact that with HD the intensity ratios OD/ZnD and ZnH/OH are much higher than that found for  $D_2$  or  $H_2$  alone. This result can be explained if we assume that two modes of adsorption of HD are possible, *viz.*



and that the first is the favored form.

When HD is admitted to a sample of zinc oxide, the spectrum changes rapidly with time at first but after about 30 min, little change occurs. These changes are accompanied by the reaction



Kinetic measurements show this reaction occurs over 1

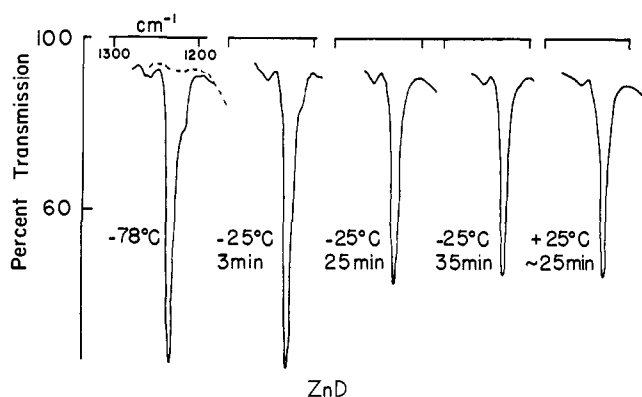


Figure 4. Changes in ZnD band from HD (70 mm) with temperature and time.

g of catalyst with a half-life of 11 min at 100 mm in a system with a volume of about 100 cc. This is in fair agreement with the reported<sup>13</sup> half-life of 7.8 min for the reverse reaction under comparable conditions at 200 mm. (Precise comparison requires data on the order of the reaction.) Figure 3 shows the change in the amount of ZnH, OD, and OH, ZnD as a function of time when 70 mm of HD are admitted to the ir cell. It is apparent from this plot that the changes in the spectrum cease when the exchange reaction is complete. It is further apparent that the bias toward formation of ZnH-OD rather than ZnD-OH *increases* with time and is, in fact, *greater* as the HD partial pressure *decreases*. This bias will represent equilibrium effects only when reaction has ceased and, to evaluate it, we need to know how much ZnH-OH and ZnD-OD are formed by direct adsorption of the H<sub>2</sub> and D<sub>2</sub> present at equilibrium. Unfortunately, the latter cannot be ascertained, but we can examine the extreme effects of such adsorption. If neither H<sub>2</sub> nor D<sub>2</sub> adsorb as such, we obtain a minimum ratio of ZnH-OD to ZnD-OH of 2.2; if the adsorption of H<sub>2</sub> and D<sub>2</sub> is comparable to that of ZnD-OH, the bias is 3.3.

The infrared spectrum of H<sub>2</sub>:D<sub>2</sub> mixtures was also examined during equilibration but not in as much detail as with HD. Results are summarized in Table I.

Table I. Infrared Spectrum of Adsorbed Hydrogen Isotopes at Room Temperature

Experiment	1	2	3	4	5	6
Gas phase	$P_{H_2} = P_{D_2} = 35$ mm	$P_{H_2} = P_{D_2} = 35$ mm	$P_{HD} = P_{HD} = 78$ mm	$P_{HD} = P_{HD} = 78$ mm	$P_{H_2} = P_{D_2} = 80$ mm	$P_{HD} = P_{HD} = 78$ mm
Exposure	298°K, 0-5 min	298°K, 30-35 min	298°K, 55-56 min	298°K, 1 hr, and cool -78°	298°K, 120 min	298°K, 1 hr
% ZnH	26	32	34	30	36	32
% OH	22	12	14	17	17	14
% ZnD	25	22	17	21	19	21
% OD	27	35	34	32	28	34

In experiment 1 the initial scan (completed within 5 min) reveals about equal amount of Zn-H, OH, ZnD, and OD. As equilibration proceeds (experiment 2) the same bias in favor of Zn-H and OD appears; as expected, this bias is about the same as that found for

(13) W. C. Conner and R. J. Kokes, *J. Phys. Chem.*, **73**, 2346 (1969).

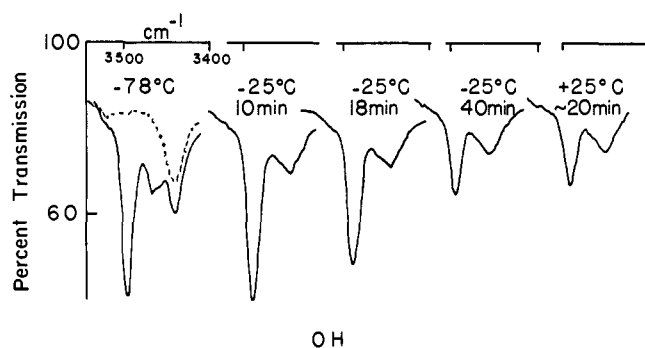


Figure 5. Changes in OH band from HD (70 mm) with temperature and time.

equilibrated HD (experiment 3). It is worth noting that the amount of OH is considerably below the amount of ZnD. Such a result is also implied by the data of Tamaru, *et al.*<sup>9</sup> This point was rechecked in experiments 5 and 6 with another sample of zinc oxide which yielded better quality spectra. Once again, equilibrated HD or H<sub>2</sub>:D<sub>2</sub> leads to the same bias favoring ZnH and OD, but the trend for the OH to be lower than ZnD remains. It is conceivable that these low values may be artifacts due to the difficulties (alluded to in the Experimental Section) in ascertaining accurately the OH intensities. Finally, in Table I, run 4, we indicate the results of analysis of the spectrum obtained when equilibrated HD is suddenly cooled to -78°. The total amount of adsorption, based on intensity data, changes less than 10% and there is a slight reduction in the bias. The change is similar even when the sample is quenched to -195°. Thus, the surface distribution is largely "frozen in." Furthermore, the similarity of the data suggests the relative infrared absorption coefficients are nearly independent of temperature, a conclusion supported by the calibration data.

**Kinetic Isotope Effects.** Infrared studies at room temperature show that both adsorption and desorption of type I hydrogen are rapid: the OH and ZnH bands appear immediately<sup>14</sup> on admission of the gas and essentially disappear after evacuation for 10 min. When the sample is first cooled to -78°, adsorption, as measured by infrared experiments, is still quite rapid but desorption is very slow; in fact, evacuation for 1 hr or more has little effect on the bands due to adsorbed hydrogen. (Similar conclusions were recently reported by Tamaru, *et al.*<sup>9</sup>) Thus, whereas at room temperature amounts of type I adsorption are controlled by thermodynamics, at lower temperatures amounts of adsorption are controlled by kinetics. Activated adsorption of type I hydrogen can be studied in the infrared even at temperatures as low as -195°. Under these conditions hydrogen adsorption at 80 mm is still rapid; on the basis of intensity data adsorption reaches about 80% of the room temperature value within 15 min after the sample is exposed to hydrogen. Adsorption of deuterium at -195° is not quite as rapid; nevertheless, adsorption reaches about 50% of the room temperature value in 15 min. In both cases, as the sample is warmed, the amount of adsorption increases, reaches a plateau at low temperatures, and shows little change as room tem-

(14) The time scale of these experiments is determined by the time for an ir scan. This requires several minutes; hence, the term "immediately" in this context means within a few minutes.

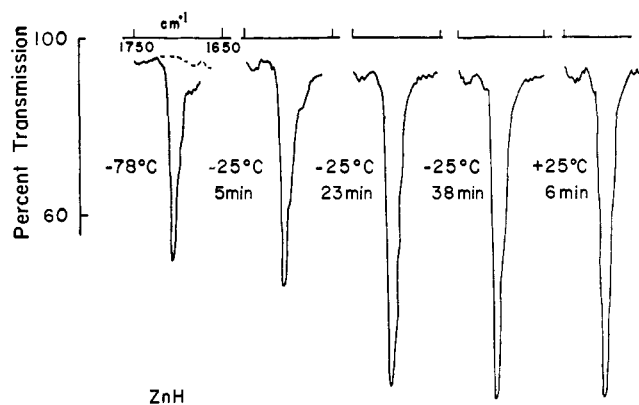


Figure 6. Changes in ZnH band from HD (70 mm) with temperature and time.

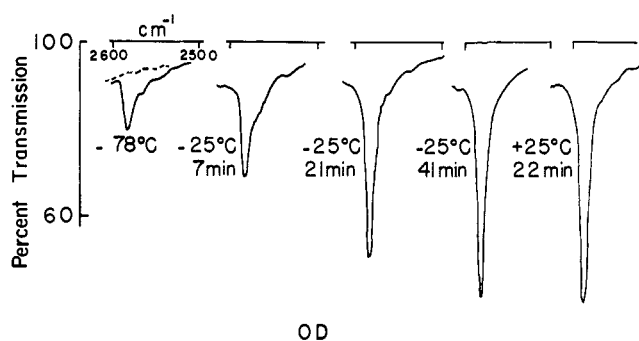


Figure 7. Changes in OD band from HD (70 mm) with temperature and time.

perature is approached. This is what one should expect in isobars for activated adsorption when the pressure is such that, at equilibrium, saturation is approached.

Figures 4–7 show the ZnD, OH, ZnH, and OD bands when zinc oxide at  $-78^\circ$  is exposed to 70 mm of HD; successive scans in these regions show how these peaks change as the sample is warmed to room temperature. (The background shown is that for room temperature.) At  $-78^\circ$ , where adsorption is kinetically controlled, the dominant species is ZnD–OH and the spectrum changes little in 30 min. When the sample is warmed to  $-25^\circ$ , changes start to occur. After about 40 min at  $-25^\circ$ , the dominant species has changed from ZnD–OH to ZnH–OD with the bias toward the latter comparable to that observed at room temperature where adsorption is thermodynamically controlled.

Since isotope effects are often dominated by a Boltzmann-like term, one would expect the kinetic isotope effect to be even more pronounced at  $-195^\circ$ . Figure 8 shows the spectrum of HD adsorbed at  $-195^\circ$ . At  $-195^\circ$  the Zn–H and OD bands are virtually absent whereas the Zn–D and OH bands are quite strong. After warming to room temperature, as expected, Zn–H and O–D become the dominant species.

(There are several features of the  $-195^\circ$  spectrum that are not seen in the spectrum at room temperature. The background band at  $3450\text{ cm}^{-1}$  sharpens and intensifies and a new band appears in the background at  $3515\text{ cm}^{-1}$ . Second, the OH band from hydrogen shows evidence of structure. This may be a result of perturbation of the new background band, but the appearance of some structure in the OD band when deu-

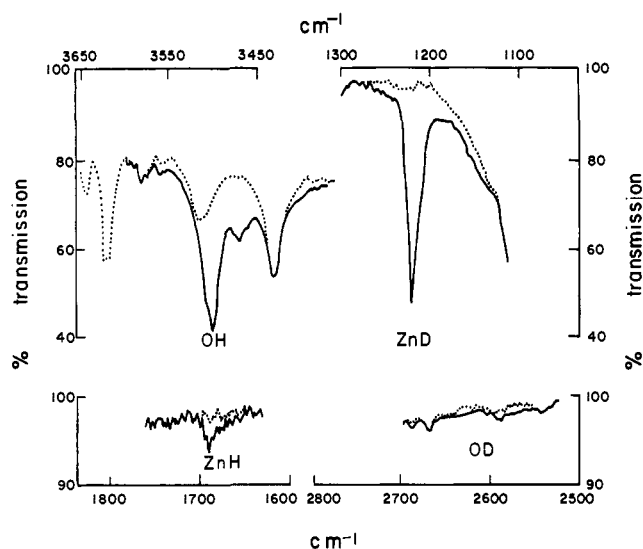


Figure 8. Spectrum of HD (80 mm) at  $-195^\circ$ .

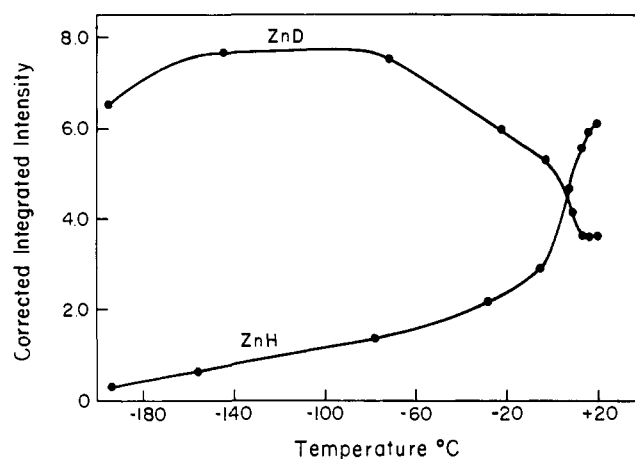


Figure 9. Changes in amounts of ZnD and ZnH from HD with temperature.

terium is adsorbed suggests that this structure is due to adsorbed species. Finally, the positions of all the bands due to chemisorbed hydrogen and deuterium shift. In a given run with HD at room temperature, the OH, ZnH, OD, and ZnD bands occurred at  $3487$ ,  $1705$ ,  $2582$ , and  $1228\text{ cm}^{-1}$ , respectively; when the sample was cooled to  $-195^\circ$ , the corresponding dominant bands occur at  $3502$ ,  $1691$ ,  $2591$ , and  $1219\text{ cm}^{-1}$ , respectively. We shall confine our remarks to the dominant bands and ignore the shifts that occur as a function of temperature.)

Figure 9 shows the changes that occur in the amounts of ZnH and ZnD as a sample at  $-195^\circ$  exposed to HD at 80 mm is warmed; similar changes occur in the corresponding OD and OH bands. The data refer to scans made at approximately 10-min intervals after the warm-up started. Above  $-144^\circ$  the sums of these amounts were relatively constant at  $8.9 \pm 0.4$  with only a slight upward trend; at  $-195^\circ$  the sums of these amounts were 80% of this figure. Thus, it would seem that below  $-144^\circ$  the latter stages of adsorption are too slow for saturation to be achieved readily. Changes in relative amounts of ZnH, OH, ZnD, and OD were slight below about  $-60^\circ$ , but the rate of

change is marked at  $-25^\circ$  as suggested by the data in Figures 4-7. Since desorption is slow at  $-25^\circ$ , these changes may occur *via* a surface rearrangement rather than adsorption-desorption *via* the gas phase.

Table II provides a quantitative summary of the results at low temperatures and the changes that occur on warm-up to room temperature. Experiment A reveals that the species formed from HD at  $-195^\circ$  is almost ex-

**Table II.** Infrared Spectrum of Hydrogen Isotopes at Low Temperatures

Experiment	A	B	C	D	E
Gas phase	$P_{HD} =$ 78 mm	$P_{HD} =$ 78 mm	$P_{HD} =$ 70 mm	$P_{HD} =$ 70 mm	$P_{H_2} =$ $P_{D_2} =$ 80 mm
Exposure	At $-195^\circ$ <sup>a</sup>	A at $25^\circ$ , 25 min	At $-78^\circ$	C at $25^\circ$ , 30 min	At $-195^\circ$
% ZnH	2	33	9	30	40
% OH	49	13	45	13	44
% ZnD	47	21	38	19	7
% OD	2	33	8	38	9

<sup>a</sup> The signal intensity for the OD band (which has a low absorption coefficient) is comparable to noise; the listed value represents a maximum value, the lower limit of which is zero. The signal intensity for the ZnH band (which has a high absorption coefficient) is about four times the noise level; hence, a ZnH species is definitely present in roughly the listed amount.

clusively ZnD-OH; values quoted for ZnH and OD can, in large part, be accounted for by the isotopic impurities in the HD (1.2% D<sub>2</sub> and 3.8% H<sub>2</sub>). Reversal of this bias by warming to room temperature is readily achieved as shown by experiment B. Experiments C and D reveal that for higher temperatures ( $-78^\circ$ ) the bias toward ZnD-OH is not as great but, once again, warming to room temperature reverses the bias. (It is worth noting that about the same distribution is achieved at room temperature in these runs as we found when the HD or H<sub>2</sub>:D<sub>2</sub> is admitted at  $25^\circ$ , *cf.* Table I.) Finally, experiment E demonstrates that there is also a sizable kinetic isotope effect at  $-195^\circ$  for hydrogen *vs.* deuterium. Adsorption experiments already described with either gas alone showed that the total amount adsorbed at  $-195^\circ$  was initially greater for hydrogen than for deuterium, but the initial stages of this adsorption were so fast that rate measurements were impractical. For this reason a competitive experiment was carried out in which a 50:50 mixture of hydrogen and deuterium was admitted to the sample at  $-195^\circ$  and the isotope effect was gauged by the relative amount of ZnH-OH and ZnD-OD formed by rapid irreversible adsorption. On this basis the rate of hydrogen chemisorption is at least  $5.3 \pm 0.4$  times as fast as deuterium chemisorption. It should be emphasized, however, that adsorption may be so rapid that it depletes the gas phase of hydrogen near the sample; in this event the estimated isotope effect represents a minimum value, and these results demonstrate only that there is a large isotope effect. This kinetic isotope effect is still evident at  $-78^\circ$ ; from competitive adsorption experiments, we obtain an estimated rate ratio of at least 2.0. (If effusion into the interstices of the pressed disk were rate controlling, one might expect a ratio of  $\sqrt{2}$  even in the absence of isotope effects. Part of the observed

ratio may arise from such effects, but the fact that the ratios are larger than  $\sqrt{2}$  suggests that the ratio is due, at least, to a kinetic isotope effect.)

## Discussion

The results can be summarized as follows.

1. Type I isotherms, as defined, are reversible only near room temperature. Such isotherms are essentially the same ( $\pm 5\%$ ) for hydrogen and deuterium; hence, type I adsorption shows no thermodynamic isotope effect ( $\pm 5\%$ ) for hydrogen compared to deuterium.

2. Type I adsorption at room temperature of HD occurs with the species ZnH-OD preferred over the species ZnD-OH. The thermodynamic isotope effect for "HD" *vs.* "DH" leads to a ratio of these species at room temperature of *at least* 2.2.

3. A kinetic isotope effect for the rate of type I adsorption is readily observable for hydrogen and deuterium at both  $-78$  and at  $-195^\circ$ . The rate for hydrogen adsorption is *at least* five times that for deuterium at  $-195^\circ$ .

4. Type I HD adsorption shows a kinetic isotope effect favoring ZnD-OH over ZnH-OD. At  $-78^\circ$  the bias is about a factor of 5; at  $-195^\circ$  it is at least 20 and (with corrections for isotopic impurities) may be as high as 100.

5. Bands for the dominant OH, ZnH, OD, and ZnD species occur at 3490, 1710, 2584, and 1232  $\text{cm}^{-1}$  at room temperature and shift little (*i.e.*, less than 20  $\text{cm}^{-1}$ ) with changes in coverage or temperature. These bands clearly stem from stretching vibrations; no bands ascribable to bending vibrations are observed above 1050  $\text{cm}^{-1}$ .

Computation of isotope effects in terms of statistical thermodynamics<sup>15,16</sup> is often simplified by cancellation of troublesome terms in the resulting ratios of partition functions for the two isotopic species. Such simplification also results in the present case. Realistic models for adsorbed species introduce nonideality by assuming nearest-neighbor interactions<sup>17</sup> or energetic heterogeneity of adsorption sites.<sup>18,19</sup> The fact that stretching frequencies for adsorbed hydrogen are independent of coverage requires that neither interactions nor heterogeneity affects the well-bottom curvature of the potential energy surface that defines these vibration frequencies. When this is true, it can be shown that (for either of these models) the equilibrium isotherm for two isotopic species A and B must satisfy the equation<sup>20</sup>

$$(P_A/P_B)_\theta = q^A_{(w)}q^B_{(n0)}/q^B_{(w)}q^A_{(n0)} \quad (1)$$

wherein the left side refers to the ratio of pressures for a

(15) J. W. Bigeleisen and M. G. Mayer, *J. Chem. Phys.*, **15**, 261 (1947).

(16) J. W. Bigeleisen and M. Wolfsberg, *Advan. Chem. Phys.*, **1**, 15 (1958).

(17) T. L. Hill, "Statistical Thermodynamics," Addison-Wesley, Reading, Mass., 1960, pp 235-258.

(18) T. L. Hill, *J. Chem. Phys.*, **17**, 762 (1949).

(19) A. Clark, "The Theory of Adsorption and Catalysis," Academic Press, New York, N. Y., 1970, p 47.

(20) The models discussed herein are useful only if the perturbation of the adsorbent due to adsorption is small. Use of such models for chemisorption has been criticized because it is asserted that severe perturbation of the surface always accompanies chemisorption. Even if this is true, we do not believe this vitiates eq 1. It is possible to introduce formally such perturbation effects into the statistical treatment; as long as these perturbations depend on the chemical species adsorbed rather than the isotopic species, the cancellation leading to eq 1 will still obtain.

fixed  $\theta$  on the isotherm and the  $q$ 's refer to partition functions for the gaseous species (g) and adsorbed species at zero coverage ( $a_0$ ). For adsorption of  $H_2$  compared to  $D_2$  this becomes

$$\left(\frac{P_{D_2}}{P_{H_2}}\right) = \frac{q_{(g)}^{D_2}}{q_{(g)}^{H_2}} \cdot \left\{ \frac{q_z^{ZnH} q_z^{OH}}{q_z^{ZnD} q_z^{OD}} \right\} \left[ \frac{q_x^{ZnH} q_y^{ZnH} q_x^{OH} q_y^{OH}}{q_x^{ZnD} q_y^{ZnD} q_x^{OD} q_y^{OD}} \right] \quad (2)$$

wherein we have factored the partition function for the adsorbed species into terms corresponding to motions perpendicular to the plane of the surface (subscript  $z$ ) and motions in the plane of the surface (subscript  $x$  and  $y$ ). The term in braces is determined by the observed stretching frequencies; the term in brackets consists of partition functions for bending modes or two dimensional translations and cannot be evaluated without further assumptions. If we evaluate the known factors in eq 2, with anharmonicity corrections for the gaseous species,<sup>21</sup> we obtain

$$(P_{D_2}/P_{H_2})_\theta = 3.85F \quad (3)$$

where  $F$  represents the term in brackets in eq 2. Since experimentally there is no isotope effect ( $\pm 5\%$ ) the ratio in eq 3 must be unity and  $F$  must be about 0.26. Computations of  $F$ , assuming bending frequencies for OH(OD) and ZnH(ZnD) similar to those found in simple molecules, lead typically<sup>22</sup> to values like 0.04; hence, we must assume the motions contributing to  $F$  are significantly different from bending vibrations in simple molecules. The maximum value for an  $F$  composed of vibrational partition functions is that obtained in the classical limit, 0.269, a value very close to that needed for agreement with experiment. Such a result would be obtained if, in the adsorbed state, bending modes became low-frequency librational modes with frequencies of the order of a few hundred wave numbers. This assumption is not without precedent; such low frequencies are observed for bending vibrations in ionic hydroxides.<sup>25-27</sup> As an alternative to the above we could assume  $F$  is composed of two-dimensional translational partition functions. In this event  $F$  becomes 0.25 and we again obtain satisfactory agreement with experiment.

Thus, we conclude that at room temperature the  $F$  in eq 3 is that appropriate for very low frequency bending vibrations or two-dimensional translation. If we make this same assumption for "HD" compared to "DH" adsorption, we find using an appropriate reformulation of eq 2 that "HD" is the preferred form for adsorbed hydrogen deuteride by a factor of 2.8, which agrees well with the observation that this is the preferred form by *at least* a factor of 2.2. More complete calculations on this same basis of the relative adsorption coefficients of HD, DH,  $H_2$ , and  $D_2$  lead to the conclusion that the ir spectrum for equilibrated HD or  $H_2$  plus  $D_2$  would

(21) G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, New York, N. Y., 1950, pp 532-533.

(22) For example, we can assume the OH bending frequency is similar to that in methyl alcohol ( $1340 \text{ cm}^{-1}$ )<sup>23</sup> and the ZnH bending frequency is similar to that for gallium hydrides ( $523 \text{ cm}^{-1}$ ).<sup>24</sup>

(23) G. Herzberg, "Molecular Spectra and Molecular Structure," Van Nostrand, New York, N. Y., 1952, p 335.

(24) D. M. Adams, "Metal-Ligand and Related Vibrations," St. Martin's Press, New York, N. Y., 1968, p 21.

(25) R. M. Hexter, *J. Chem. Phys.*, **34**, 941 (1961).

(26) N. Acquista and S. Abramowitz, *ibid.*, **51**, 2911 (1969).

(27) R. A. Buchanan, H. H. Caspers, and J. Murphy, *Appl. Opt.*, **2**, 1147 (1963).

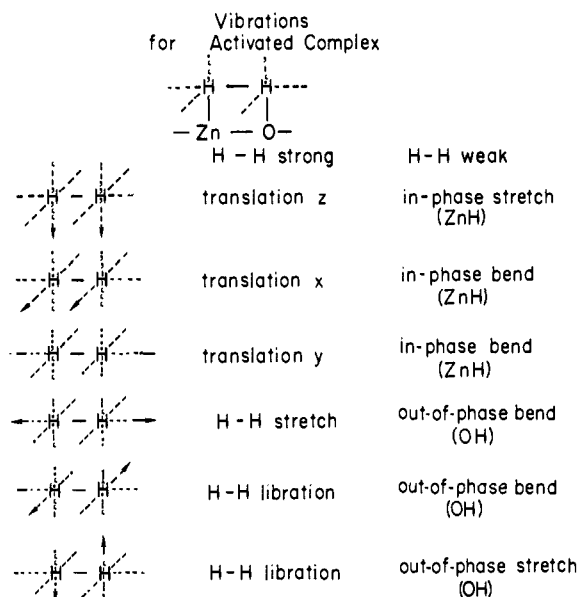


Figure 10. Normal modes for adsorbed hydrogen in strong and weak bond limits.

yield bands corresponding to 64% ZnH and OD compared to 36% ZnD and OH. This is in good agreement with the observations summarized in Table I and II. Thus, this single assumption regarding the form of  $F$  in eq 3 rationalizes not only the observed equilibrium isotope effect for  $H_2$  vs.  $D_2$  but also the observed preferential adsorption of "HD."

The ratio of adsorption rate constants for two isotopic species, 1 and 2, is given by the following expression

$$k_1/k_2 = (Q_1^\ddagger/Q_2^\ddagger)(Q_2/Q_1) \quad (4)$$

where  $Q$  and  $Q^\ddagger$  are partition functions for the reactant and activated complex, respectively. In order to utilize this equation we must assume a form for the activated complex including its vibrational spectrum and we must identify the reaction coordinate.<sup>28</sup> Clues to this are offered by the characteristics of the hydrogen chemisorption. The bond energy for a hydrogen molecule is about 100 kcal and the estimated heat of adsorption is about 10 kcal. Since the activation energy for adsorption is less than 5 kcal, adsorption must occur *via* a concerted mechanism. In other words, in the activated complex hydrogen is already strongly bound to the Zn-O pair site.

Figure 10 depicts the vibrations of such an activated complex in the limits where the H-H bond is strong and weak, respectively. (We treat surface atoms as if they had infinite mass.) In the limit of a strong hydrogen-hydrogen bond, the reaction coordinate, *i.e.*, the normal mode resulting in the most precipitous descent on the potential energy surface,<sup>29</sup> would be either an H-H stretch or  $z$  translation. The isotope effect stems from differences in reduced mass for the remaining vibrations. For HD and DH such differences would not occur for this model and no isotope effect for these species should be observed. Thus, the large isotope effect for HD vs.

(28) L. Melander, "Isotope Effects on Reaction Rates," Ronald Press, New York, N. Y., 1960.

(29) For a recent discussion, see D. G. Truhlar and A. Kuppermann, *J. Amer. Chem. Soc.*, **93**, 1840 (1971).

DH suggests the H-H bond in the activated complex is not strong. In the limit where the H-H bond becomes very weak, we can view the vibrations of such a complex as coupled Zn-H and OH vibrations, wherein out-of-phase stretching is mostly an OH stretch and in-phase stretching is mostly a Zn-H stretch. The OH stretch is nearly twice the frequency of the ZnH stretch; hence, it would seem that shortening of the OH bond corresponds to the most precipitous descent on the potential energy surface, *i.e.*, the out-of-phase stretch is the reaction coordinate. Then, in the limit where the H-H bond is very weak, we can estimate the kinetic isotope effect on the basis of procedures paralleling those used to compute equilibrium isotope effects.<sup>30</sup> Such computations yield rate ratios of 80 and 6 at  $-195$  and  $-78^\circ$ , respectively. This compares reasonably well with the experimental results: 20-100 at  $-195^\circ$  and 5 at  $-78^\circ$ .

Computations reveal that the rate ratio for DH *vs.* HD should be about 3 even at room temperature. Accordingly, if zinc oxide is exposed to HD at room temperature, we should find ZnD-OH dominant initially, but, as equilibrium is approached, ZnH-OD should become the dominant form since it is favored by the equilibrium isotope effect. We believe Figure 3 shows the latter stages of this effect inasmuch as the ZnH-OD bias is least initially (when the partial pressure of HD is greatest). Such behavior suggests that near  $t = 0$  the equilibrium bias is offset by the opposite kinetic bias.

For quantitative estimates we must utilize the foregoing procedures. The dominant features that give rise to the observed kinetic and equilibrium isotope effects with hydrogen deuteride, however, are more sharply defined in a qualitatively correct discussion based only on zero point energies wherein bending vibrations are assumed to be of such low frequency that they can be ignored. Let  $q_0$  be the energy difference between the bottom of the potential energy curves for gaseous HD and that for the adsorbed species. Then,  $q$ , the heat of adsorption at  $0^\circ\text{K}$ , is given by

$$q_{\text{HD}} = +q_0 + \frac{1}{2}h\nu_{\text{HD}} - \frac{1}{2}h\nu_{\text{ZnH}} - \frac{1}{2}h\nu_{\text{OD}}$$

$$q_{\text{DH}} = +q_0 + \frac{1}{2}h\nu_{\text{HD}} - \frac{1}{2}h\nu_{\text{ZnD}} - \frac{1}{2}h\nu_{\text{OH}}$$

The  $q$  that is greater will identify the more strongly adsorbed form. Consider the difference in these two heats

$$q_{\text{HD}} - q_{\text{DH}} = (\frac{1}{2}h\nu_{\text{OH}} - \frac{1}{2}h\nu_{\text{OD}}) - (\frac{1}{2}h\nu_{\text{ZnH}} - \frac{1}{2}h\nu_{\text{ZnD}})$$

(30) The assumption that bending frequencies are so low that they approach the classical limit undoubtedly fails at  $-195^\circ$ . For computations of isotope effects for  $\text{H}_2$  *vs.*  $\text{D}_2$  this failure introduces serious errors; nevertheless, all reasonable approximations suggest that the isotope effect is normal as observed. For HD *vs.* DH the error introduced by this assumption is not as serious because both the numerator and denominator in the last factor of eq 2 (*mutatis mutandis*) contain partition functions for both light and heavy isotopes; this form means that the contribution of this factor to isotope effects is relatively small even for nonclassical partition functions so that the calculations should be reasonably reliable.

Both terms in parentheses are positive but the first term, which involves the higher frequency OH (and OD), will always be dominant; hence, the heat of adsorption of HD,  $q_{\text{HD}}$ , is larger than that of DH,  $q_{\text{DH}}$ , and HD adsorption is the dominant form. For the kinetic isotope effect let  $E^\ddagger$  be the well-bottom to well-bottom activation energy. Activation energies are given by

$$E_{\text{HD}}^\ddagger = E^\ddagger + \frac{1}{2}h\nu_{\text{ZnH}} - \frac{1}{2}h\nu_{\text{HD}}$$

$$E_{\text{DH}}^\ddagger = E^\ddagger + \frac{1}{2}h\nu_{\text{ZnD}} - \frac{1}{2}h\nu_{\text{HD}}$$

where we have omitted the OH(OD) frequency because it is assumed to be the reaction coordinate. The preferred (more rapidly reacting) form will be that with the lower  $E^\ddagger$ . Consider the difference

$$E_{\text{HD}}^\ddagger - E_{\text{DH}}^\ddagger = \frac{1}{2}h\nu_{\text{ZnH}} - \frac{1}{2}h\nu_{\text{ZnD}}$$

The term on the right is positive; hence,  $E_{\text{DH}}^\ddagger$  is lower and DH is the preferred form. Similar arguments can be made for  $\text{D}_2$  *vs.*  $\text{H}_2$ . For  $\text{H}_2$  *vs.*  $\text{D}_2$  the computed difference in  $q$  values is only 190 cal; for HD *vs.* DH this difference is 600 cal. At room temperature the  $\text{H}_2$ - $\text{D}_2$  value is less than one-third  $RT$  whereas the HD-DH value is slightly greater than  $RT$ . Since the equilibrium isotope effect depends (roughly) exponentially on these values, we would expect a large HD-DH effect and a small  $\text{D}_2$ - $\text{H}_2$  effect. Parallel arguments lead to the observed normal  $\text{H}_2$ - $\text{D}_2$  kinetic isotope effect.

Three conclusions may be drawn from this research.

1. The detailed computations of kinetic and equilibrium isotope effects for adsorption of type I hydrogen are, of course, approximate. Nevertheless, the computations yield a consistent interpretation of the data with assumptions that are based either on experimental facts or models deemed plausible by tradition. Thus, it seems reasonable to suppose that the cancellation of complexities often found in similar computations for homogeneous systems may also carry over to heterogeneous systems.

2. The existence of sizable kinetic isotope effects for HD *vs.* DH and  $\text{H}_2$  *vs.*  $\text{D}_2$  demonstrates that the slow step for type I hydrogen is not a process characteristic of the solid alone as has been concluded for the "slow chemisorption" of hydrogen.

3. Finally, the isotope effects (kinetic and equilibrium) favoring ZnD-OH or ZnH-OD provide compelling evidence that hydrogen adsorption actually occurs on Zn-O pair sites, as suggested. This conclusion is a primitive one and is independent of any explanation of the source of these isotope effects.

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