THE ADSORPTION AND ORTHO–PARA CONVERSION OF HYDROGEN ON DIAMAGNETIC SOLIDS. II. THE RELATIVE ADSORBABILITIES OF ORTHOHYDROGEN AND PARAHYDROGEN

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It is shown that orthohydrogen is more strongly adsorbed than parahydrogen when physically adsorbed on TiO_2 or charcoals. A separation factor of about 1.6 is observed with TiO_2 at $-183°$. The effect of the preferential adsorption on the kinetics of the ortho–para conversion is demonstrated. It may be obscured by a lag in the establishment of the adsorption equilibrium. The separation effect is explained as being principally due to hindered rotation.

In liquid and solid hydrogen the para-modification has a higher vapor pressure than the ortho-modification.[2] Ubbelohde[3] inferred from his experiments on the composition of hydrogen desorbed from charcoal at 90°K. that a similar effect may exist in case of adsorbed hydrogen. However, no reproducible results could be obtained by his technique. The ortho–para separation effect has so far generally been assumed to be too small to have an appreciable effect on the kinetics of the ortho–para conversion on solids or on the adsorption equilibrium. In the following some experiments are described which establish the existence and magnitude of the preferential adsorption of orthohydrogen in some cases.

The adsorption and conversion of ortho–para mixtures at low temperatures was studied with TiO_2 (rutile) and charcoals of high surface area. In these cases the observed conversion appears to be of the magnetic type[2b,4] involving adsorbed hydrogen molecules. Mainly two kinds of experiments were performed: (1) Kinetic experiments: if the estab-

lishment of the adsorption–desorption equilibrium is fast enough, a change of the gas phase composition is to be expected immediately after contacting the gas with the surface. (2) Equilibrium experiments: the gas was allowed to come to a complete ortho–para equilibrium in presence of the catalytic surfaces. It was then very rapidly desorbed and its composition determined.

Experiments and Results

The ortho–para analysis was carried out by means of the Farkas micromethod.[2b] The stability of the cell was carefully checked before and during each experiment by alternate measurement of hydrogens of known concentration. The error of measurement of a given para concentration (in %) is less than 0.4. The experimental set-up for measuring the conversion and for the volumetric determinations was the same as described in the preceding paper.[4]

Materials.—3.42 grams of titanium dioxide (rutile) was used in a reaction vessel, leaving a void space of 8.84 cc. It was the same sample as used in the previous investigation ("TiO_2 II").[4] It had been carefully outgassed at 350°, and then had been contacted with oxygen at room temperature. By this latter treatment the conversion half-life at 90°K. increased by a factor 4.5. The adsorption isotherms at 77.5 and 90.2°K. were measured. These were taken with equilibrium hydrogen prepared by desorption from charcoal at the corresponding temperature. The isotherms were not linear; the isosteric heats decreased with coverage. At 5.0 cc. coverage (1.46 cc./g.; about 5×10^{-3} monolayers) the isosteric heat is about 2.1 kcal.

Maple wood charcoals and a sugar charcoal were carefully outgassed at 200°. With sugar charcoal a coverage of 6 cc. per gram of coal was used giving an equilibrium pressure of 1.3 mm. at 77.7°K. The heat of adsorption at this coverage was about 1.1 kcal./mole.

Kinetic Experiments.—In the lower section of Fig. 1 a typical conversion curve is shown obtained at 77.5°K. when contacting normal hydrogen (25% parahydrogen) with TiO_2. About 6.5 cc. (STP) was adsorbed, giving an equilibrium pressure of about 3.5 mm. The system was allowed to come to an approximate pressure equilibrium by leaving the tap of the reaction vessel open for about 20 seconds. After closing the tap, any subsequent changes in the adsorption equilibrium may have somewhat changed the equilibrium pressure in the vessel, but not the coverage, because practically all the gas in the reaction vessel was in the adsorbed phase (98% at equilibrium). In the present case, there seems to be no immediate change of the gas phase composition on contacting the gas with the surface. However, the relative rate of change of the gas composition appears greatly increased during the initial period of the conversion. The equilibrium concentration at the given temperature is 50.0% parahydrogen.[2b] The excess over this concentration sinks to one-half of its original value within the first 3.5 minutes; then it decreases again to half within about 8 minutes.

The effect of the ortho–para separation becomes much more striking when one observes the conversion in the reverse direction. Conversion and separation then act in opposite directions. In the upper part of Fig. 1 the results of two runs are plotted in which 68% parahydrogen was contacted with the surface, again for 6.5 cc. gas and 77.5°K.
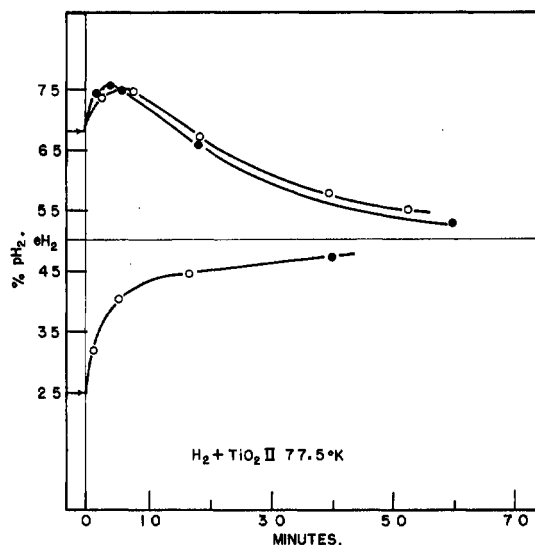

Fig. 1.—The conversion of 68% parahydrogen (upper curves) and normal hydrogen (lower curve) to equilibrium hydrogen on TiO_2 II at 77.5°K.

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(2) (a) K. F. Bonhoeffer and P. Hartek, *Z. physik. Chem.*, **B4**, 113 (1929); (b) *cf.* A. Farkas, "Orthohydrogen, Parahydrogen and Heavy Hydrogen," Cambridge University Press, 1935.

(3) A. R. Ubbelohde, *Trans. Faraday Soc.*, **28**, 291 (1932).

(4) Y. L. Sandler, THIS JOURNAL, **58**, 54 (1954).

As the desorption of the gas at this temperature was rather slow, the previously adsorbed hydrogen was pumped off at a higher temperature and the reaction vessel was then cooled *in vacuo* to 77.5°K. This method of cooling probably was not quite effective. After admission of the parahydrogen from the measuring buret, the tap of the reaction vessel was left open for about 12 seconds to allow the pressure equilibrium to be approximately established. The curve marked by open circles was so obtained. Before the second run was made (full circles), the gas was pumped off as previously, but the powder was cooled in 1-2 mm. helium for 1 hour. The tap was left open for 20 seconds when contacting with the parahydrogen. The total depletion of the adsorbed gas through the successive amounts of gas withdrawn for analysis, was less than 1%. The curves are seen to rise to a maximum para concentration of about 75% (due to the separation effect), before falling off (due to the ortho–para conversion). There is a time lag of 4 to 6 minutes before the maximum separation is reached.

Similar experiments were performed at 90.2°K. To attain the temperature equilibrium of the powder, in this case the powder was first contacted with hydrogen which was then removed by pumping for half an hour. 2.7 cc. of 68% parahydrogen was adsorbed giving an equilbrium pressure of 5.5 mm. The results of two runs are shown in Fig. 2. Here log u_t/u_0 is plotted against time; u_t is the excess para concentration over the equilibrium para concentration in the gas phase at the time t, and u_0 is the excess concentration before contacting the gas with the powder. The points are seen to lie on a good straight line. There is no evidence for the existence of an initial lag, as observed at the lower temperature. In absence of a separation effect and a lag period for the establishment of the adsorption equilibrium, one would expect a straight line starting from log $u_t/u_0 = 0$ at $t = 0$. The equation of the found conversion curve is log $u_t/u_0 = -kt + 0.138$ with $k = \ln 2/\tau$ and half life $\tau = 13$ minutes. The initial concentration was 68%, the equilibrium concentration at 90.2°K. is 42.6%[2b]; from this the intercept at $t = 0$ is found to correspond to 77.5% parahydrogen.

The results are conveniently expressed in terms of a separation coefficient

$$s = (N_p/N_0)_{gas}/(N_p/N_0)_{ads} \qquad (1)$$

where N_p and N_0 are the nunber of para and ortho molecules, respectively. s is a constant at constant temperature, if Henry's law is valid. In case of a non-linear isotherm, however, as found in the present case, s may be expected to vary somewhat with composition and coverage.

The para concentration of the adsorbed phase after contact was somewhat below the admitted para·concentration of 68% due to the fact that in the present case only 93% of the gas was adsorbed. Allowing for this, we obtain from equation 1

$$s = (77.5/22.5)/(67.4/32.6) = 1.67$$

This value may be slightly too high, if any initial lag exists also in the present case. The lag must be shorter than 1.45 minutes, the time after which the first point on the curve was taken. From this point we find that s must be greater than 1.42.

In Fig. 3 is given a logarithmic plot of a conversion curve obtained with sugar charcoal when contacting normal hydrogen at 77.7°K. and 1.3 mm. pressure. There is no clear indication of a separation effect at zero time. However, the relative rate of change of the para concentration in the first two minutes is faster than later. It seems that we have here again a case similar to that described for TiO₂ (Fig. 1, lower curve), though less distinct. There appears to be a lag in the establishment of equilibrium which masks the separation effect.

Equilibrium Experiments.—In Table I the results of some experiments are summarized in which the equilibrium concentrations in the adsorbed phase at 90.2°K. were determined. A known amount of hydrogen in these experiments was first allowed to come to a complete ortho–para equilibrium. The adsorbed gas was then desorbed as rapidly as possible by connecting the powder vessel for a short measured time to an evacuated volume of 1 liter and by heating the vessel to room temperature. In some cases a pressure reading was taken by means of a gage[4] connected to the large volume; it was later compared with a second reading

after desorbing the remaining gas completely. The relative amount desorbed during the experiment was so determined (last column, Table I). In column 8 of Table I the para concentration of the adsorbed gas is given; it is assumed to be equal to the composition of the collected gas, a small correction only being applied for the gas coming from the gas phase in the reaction vessel.
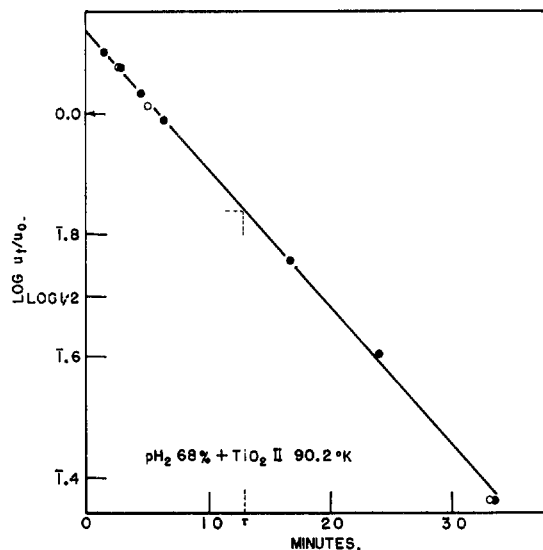
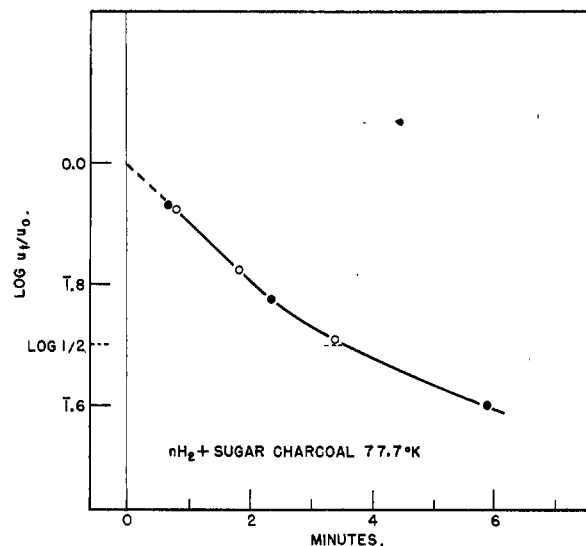Fig. 2.—The conversion of 68% parahydrogen on TiO₂ II at 90.2°K.

Fig. 3.—The conversion of normal hydrogen on sugar charcoal at 77.7°K.

The value $s = 1.30$ found for TiO₂ (Table I, row 1) is lower than the value 1.67 found in the corresponding kinetic experiment. This should be largely due to the incompleteness of the desorption. As the free energy of desorption for parahydrogen is smaller than for orthohydrogen, it might be expected that the former desorbs faster than the latter.

The following qualitative experiment showed that this actually is the case. The admitted gas was first allowed to equilibrate on the powder at 90°K. Then part of the adsorbed gas was withdrawn by connecting the reaction vessel (this time remaining at the low temperature) to evacuated volumes of varying size for a short time. A sample of the gas in contact with the powder was then rapidly withdrawn for analysis. It was found that the larger the amount of gas rejected before taking the sample for measurement, the lower was the para concentration in the measured hydrogen. This proves the faster desorption of parahydrogen. The lower value of s found on incomplete desorption is thus explained.

TABLE I

Catalyst	Temp., °K.	Equilibr. pressure, mm.	H₂ adsorbed, %	Conversion half-life, min.	Desorption time, sec.	Para concentration, % Gas phase	Para concentration, % Adsorbed phase	Separation factor, s	Remarks
TiO₂	90.2	5.5	93	13	15	42.6	36.4	1.30	Only 76% desorbed
Maple wood charcoal	77.5	~50	~100	14	~15	50.0	47.3	1.1	Desorption incomplete
	77.5	1.5	~100	6	~15	50.0	47.7	1.1	
Sugar charcoal	77.7	1.35	~100	>3	3	50.0	47.0	1.13	
	77.7	1.35	~100	>3	6	50.0	46.4	1.16	99.4% desorbed

In rows 2 and 3 of Table I the results of equilibrium experiments with a maple wood charcoal are given. This charcoal had been previously used for producing parahydrogen by the static method.[2b] It had been noticed with this and other charcoals that the gas obtained after rapid desorption always had a para concentration somewhat lower than the corresponding equilibrium concentration in the gas phase, even if the conversion half-life was as long as in the present case. The separation factor is seen to be of the order of 1.1 at 77°K. for the charcoals investigated here.

The experiments with the sugar charcoal were carried out under better controlled conditions. 0.273 gram of coal was placed in a very thin-walled vessel of only 3.5 mm. diameter thus ensuring a rapid heat transfer on desorption. Desorption was carried out by dipping the vessel into an alcohol-bath at room temperature. 1.63 cc. (S.T.P.) of hydrogen was adsorbed at 77.7°K. giving an equilibrium pressure of 1.35 mm. As seen from the data in Table I, desorption was practically complete after 6 seconds. The error of measurement in the para percentage was less than 0.2.

The time of desorption was small compared with the conversion half life; also the major part of the gas was desorbed in an even shorter time. It therefore is improbable that the reconversion due to the warming up of the catalyst had an appreciable effect on the observed para concentration. However, the possibility of a certain influence of this effect on the obtained value of s cannot be completely excluded.

The results obtained with charcoal are much less striking then the results with TiO₂, and the conclusions are less certain. In view of the similarity of the observed phenomena the interpretation of the measurements with charcoal is probably correct.

Discussion

The observed initial time lag in some of the kinetic experiments cannot be due to slowness of the diffusion in the gas phase. This is seen when comparing the conversion curves for TiO₂ at 77.5°K. and 90.2°K. (Figs. 1 and 2). The time required for the establishment of the equilibrium is much shorter at 90° although the pressure is higher. The observed lag indicates that the rate of ad- and desorption is fast at 90°K. but becomes comparable with the conversion rate at 77°K. The rapid change of the lag period with temperature indicates the existence of high barriers to migration of the gas in the surface. The values $s = 1.67$ found for TiO₂ at 90°K. may still be assumed to be roughly equal to the true equilibrium value.

We would suggest that the observed preferential adsorption of orthohydrogen is largely due to hindered rotation of the adsorbed hydrogen. However, there may be other contributing factors[3,5] such as a greater polarizability of a rotating molecule as compared with a non-rotating one (parahydrogen in the lowest rotational state).

We shall estimate the order of magnitude of the influence of hindered rotation on s by assuming

(5) K. Cohen and H. C. Urey, J. Chem. Phys., 7, 157 (1939).

that the hydrogen in the surface can be approximated by a plane rotator.

Then solely on the basis of a change in the rotational states, i.e., neglecting the interaction with vibrations and the influence of configurational effects—we expect a separation factor given by

$$s = (f_p/f_0)_{gas}/(f_p/f_0)_{ads}$$

where f_p and f_0 are the rotational partitional functions of parahydrogen and orthohydrogen, respectively.

We consider here the ground states only. At 90°K. this leads to a value for s only 3% different from the value found when taking the complete functions.

Then $(f_p/f_0)_{gas} = 1/(9 \exp [-\epsilon_1/kT])$,[2b] where $\epsilon_1 = 338$ cal./mole is the energy difference between the rotational states in the gas phase with $j = 0$ and $j = 1$. In the adsorbed phase $(f_p/f_0)_{ads} = 1/(6 \exp [-\epsilon_1/2kT])$.[6]

Therefore $s = {}^2/_3 \exp [\epsilon_1/2kT]$. At 90°K. this leads to $s = 1.7$, which is of the correct order of magnitude.

Similarly, assuming that the partition function of the resulting oscillation is $= 1$, a completely hindered rotation in the surface would lead to $s = {}^1/_3 \exp [\epsilon_1/kT] = 2.2$ at 90°K.

In view of the difference in adsorbability of the two modifications, the adsorption isotherm of hydrogen will somewhat depend on its composition. The difference in adsorption found for orthohydrogen and parahydrogen on charcoal seems to be of the same order as the difference found for hydrogen and deuterium[7]; it may be greater in other cases. In order to avoid a change in composition by conversion in the course of an adsorption experiment, it may be the simplest procedure to use hydrogen previously equilibrated at the same temperature.[8]

The present experiments suggest the use of the

(6) The partition function of a "2-dimensional parahydrogen" according to the plane rotator model would be (cf. H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry," John Wiley and Sons, New York, N. Y., 1944, p. 75)

$$f_p = 1 + 2 \sum^m \exp [-m^2\epsilon'/kT] \text{ with } m = 2, 4, 6 \dots$$

similarly, including a factor 3 for the nuclear spin degeneracy of orthohydrogen

$$f_0 = 6 \sum^m \exp [-m^2\epsilon'/kT] \text{ with } m = 1, 3, 5 \dots$$

$\epsilon' = \epsilon_1/2$.

(7) W. v. Dingenen and A. v. Itterbeck, Physica, 6, 49 (1939).

(8) This procedure is not quite correct as the equilibrium composition required depends on the value of s of the adsorbent and the fraction of gas adsorbed. In most cases, however, this will cause errors beyond the usual accuracy of adsorption experiments.

separation effect for preparing orthohydrogen or paradeuterium. The method should be considerably simpler and more efficient than the fractional distillation of liquid hydrogen. These modifications are at equilibrium at no temperature in the gas phase in concentrations greater than 75%

(orthohydrogen) and 33⅓% (paradeuterium), and they have so far not been prepared in pure form.

INFRARED SPECTRA OF ALUMINUM SOAPS AND SOAP-HYDROCARBON GELS[1]

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Contribution from the Walker Laboratory of Rensselaer Polytechnic Institute and Chemical Corps Chemical and Radiological Laboratory

Comparison of the infrared spectra of aluminum hydroxylaurate and aluminum deuteroxylaurate, and the spectra of aluminum hydroxy-2-ethyl-hexanoate and aluminum deuteroxy-2-ethyl-hexanoate showed that absorption at 2.7 μ in aluminum hydroxy soaps, ascribed to free OH, is replaced by absorption at 3.67 μ in aluminum deuteroxy soaps, the spectra of soaps of the corresponding acid being otherwise similar. Absorption at 10.14μ in aluminum soaps was shifted to 10.24μ for gallium laurate and to 10.31μ for indium laurate. The spectra were otherwise similar, except for small shifts in the 6.33μ absorption band of aluminum soaps. Absorption at 10.14μ in aluminum soaps was ascribed to the aluminum–oxygen linkage. When infrared absorption at 2.7μ is shown by aluminum soaps, it occurs also in the aluminum soap–cyclohexane gels, indicating that gelation is independent of bonded hydroxyl. Intensity of absorption at 10.14μ for a series of gels of constant concentration of aluminum dilaurate in benzene was found to decrease with the amount of added m-cresol, showing that modification of the bond in aluminum soaps causing absorption at 10.14μ is associated with loss in viscosity of gels caused by cresols.

Introduction

It has been suggested by Alexander and Gray[2,3] that aluminum soaps are made up of linked aluminum–oxygen octahedra with fatty acid chains extended from the main chain, two carbonyl groups occupying four of the coördinating positions while the two remaining positions contain hydroxyl ions, shared to form a chain. McGee[4] has pointed out that such a structure yields polymer chains which must end in charged groups. He has proposed that the adjacent disoap chains are held together by both van der Waals forces between the hydrocarbon chains and by hydrogen bonds between the hydrogen of the shared hydroxyl ions and the oxygen atoms of the carboxyl groups. In contradiction with this proposal, infrared absorption measurements[5] have shown that aluminum disoaps have a free hydroxyl group. McRoberts and Shulman[6] proposed a structure of aluminum disoaps similar to that of Gray and Alexander, and assumed that aluminum soap–hydrocarbon gels are made up of a dispersion of large soap molecules held together by hydroxyl bonds and van der Waals attraction of long hydrocarbon chains.

In view of the theories outlined, it appeared important to investigate further the assignment of absorption at 2.7 μ in aluminum disoaps to free hydroxyl,[5] and to compare the infrared absorption of aluminum disoaps and their corresponding spectra in soap–hydrocarbon gels. Since infrared absorption at 3.67 μ has been ascribed to the presence of the free deuteroxy group,[7] the preparation of aluminum deuteroxy soaps was undertaken for comparison with aluminum hydroxy soaps of corresponding fatty acids. Gallium and indium soaps were prepared from lauric acid with the expectation that a study of their infrared spectra, together with that of aluminum laurate, would aid in identifying the group contributing to the absorption at 10.14 μ, which has been shown to be characteristic of aluminum soaps. A study of the viscosities of a series of aluminum soap gels of fixed soap concentration in toluene containing m-cresol showed progressive weakening of the gel structure as the amount of m-cresol present increased.[8] An investigation of the infrared absorption spectra of such a series was made, in an attempt to identify the aluminum soap bonds causing gelation from the changes in the infrared absorption as the gel structure was modified.

Experimental

Fatty Acids.—Stearic and palmitic acids were purified by repeated recrystallizations. Lauric and myristic acids were Eastman Kodak, White Label grade. The 2-ethylhexanoic acid was Eastman Kodak, Yellow Label grade. It was treated by saponification, benzene extraction of non-saponifiable matter, conversion to the acid, and fractional distillation at 5 mm. pressure. Purity of the acids was checked by determination of the melting point, neutralization equivalent, long spacings found from pinhole X-ray diffraction measurements, analysis of the silver salts and the long spacings found by X-ray diffraction measurements on the silver salts. The results are shown in Table I. The powder X-ray diffraction patterns were obtained with a General Electric XRD-3 instrument using copper $K\alpha$ radiation.

Preparation and Analyses of Soaps.—Aluminum hydroxy soaps were prepared by addition of aluminum sulfate solu-

(1) Study conducted under contract between the Chemical Corps, U. S. Army and Rensselaer Polytechnic Institute.

(2) A. E. Alexander and V. R. Gray, *Proc. Roy. Soc. (London)*, **200**, 165 (1950).

(3) V. R. Gray, *Trans. Faraday Soc.*, **42B**, 197 (1946).

(4) C. G. McGee, *J. Am. Chem. Soc.*, **71**, 278 (1949).

(5) W. W. Harple, S. E. Wiberley and W. H. Bauer, *Anal. Chem.*, **24**, 635 (1952).

(6) T. S. McRoberts and J. H. Shulman, *Nature*, **162**, 101 (1948).

(7) Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1947, p. 335.

(8) H. Jackson, Ph.D. Dissertation, Rensselaer Polytechnic Institute, 1951.