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Gas Chromatographic Determination of Reversible Adsorption of Hydrogen

I. Reversible Adsorption over a Nickel Catalyst

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The rapid and reversible part of the stationary adsorption of hydrogen over nickel-kieselguhr (50 wt%) was determined by means of a gas chromatographic technique. The retention time of a deuterium pulse was measured at various temperatures from −195° up to 300°C using hydrogen as a carrier gas. The total uptake of hydrogen was measured separately in a static system. The extent of the reversible part of the total uptake was estimated from the deuterium retention. The isobar of the retention was similar to an ordinary adsorption isobar. The adsorption state at low temperature is suggested to be molecular.

INTRODUCTION

Hydrogen adsorption is an important elementary step involved in catalytic hydrogenation and is often considered a rapid and reversible step. When we place a hydrogenation catalyst in a hydrogen stream, and if a dynamic equilibrium of hydrogen adsorption is established, each hydrogen molecule is expected to repeat adsorption and desorption as it proceeds along the catalyst bed, although the repetition is undetectable with ordinary means.

There exists, however, a simple way to detect this dynamic equilibrium. That is, if a certain amount of adsorbed hydrogen is in a dynamic equilibrium with gaseous hydrogen over a catalyst packed in a gas chromatographic column, a pulse of deuterium should give a retention time larger than that of a nonadsorbing gas such as helium, although the pulse of hydrogen can not give any retention. Moreover, the extent of retention time is a measure of the dynamically adsorbed amount of hydrogen, which is not always equal to the total amount of adsorbed hydrogen.

An experimental verification of this prediction has not been reported for any catalyst. Hence it was decided to study the deuterium tracer chromatogram over metallic catalysts. First of all, the work was done with a nickel catalyst under atmospheric pressure and this is reported here. The work with other catalysts will be reported in successive papers.

EXPERIMENTAL

Apparatus. The apparatus is similar to that employed in conventional gas chromatography, as shown in Fig. 1. It consists of

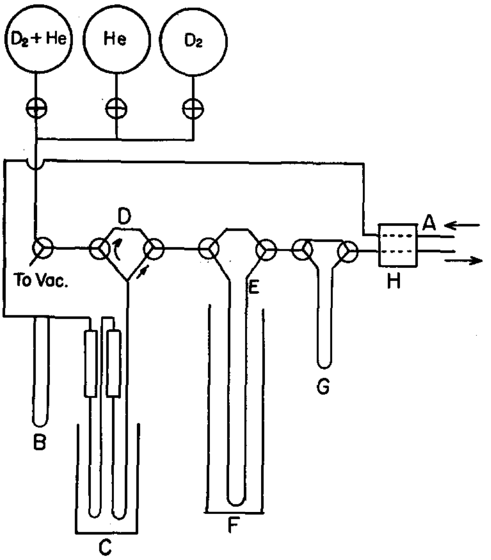

FIG. 1. Flow diagram of the apparatus: A, carrier gas inlet; B, oriffice flow meter; C, hydrogen purifier; D, doser; E, catalyst column; F, thermostat; G, analysis column; H, detector.

a carrier gas source (A), a sample doser (D) made of two glass cocks, a catalyst column (E), an analysis column (F), and a detector (H). The catalyst column is made from a glass U-tube 6 mm in inner diameter, and maintained at the desired temperatures by means of constant temperature baths, employing a fluidized bed above room temperature. The detector is a thermal conductivity cell set in a block of stainless steel and maintained at room temperature. The filament in the detector is made of platinum. In order to test the catalytic effect of the filament, a mixture of HD and D_2 (10% HD) carried by H_2 stream was passed through the detector in its operating condition. No change in the composition was observed.

Procedure. A sample of deuterium gas containing 20% helium is introduced to the purified hydrogen carrier gas which is led to the catalyst column, the analysis column, and the detector in that order. The retention time of the deuterium peak relative to helium is measured first and then the composition of the deuterium peak is obtained. The amount of one sample was about 3 ml. The flow rate of carrier gas was about 25 ml/min, varying a little case by case.

Analysis. The composition (HD–D_2) of effluent pulse from the catalyst column was determined by gas chromatography using molecular sieve 5A column at −195°C (*1*). The correction factor to the peak area was taken as 0.5 for D_2 on the basis of 1.0 for HD. This value was obtained from the calibration by means of mass spectrometry, as exemplified in the following:

Sample number:	1	2
Mole ratio $(D_2/HD)_M$ det'd. by mass spectrometry	0.48	0.55
Peak area ratio $(D_2/HD)_A$ obsd. by chromatography	0.93	1.06
$[D_2/HD]_M/[D_2/HD]_A$	0.52	0.52

Reagents and Catalyst. The hydrogen used as the carrier gas was obtained from a commercial cylinder and freed from oxygen by passing it over a palladium catalyst at 300°C followed by drying with a Dry Ice trap. Deuterium gas was supplied by Showa Denko Co. and reported by them to be 99.65% deuterium. The catalyst used was Stabilized Nickel Catalyst #101 of 40–60 mesh grains supplied by Nikki Kagaku Co. and reported by them to be composed of 50% nickel and 50% kieselguhr. It was once reduced but stabilized by the supplier. Before the measurement it was reduced with flowing hydrogen at 350°C for 12 hr and kept all the time in an atmosphere of hydrogen. The surface area of the reduced catalyst was measured by the BET method as 91 m^2/g and the volume of carbon monoxide chemisorbed at −183°C was 7.6 ml/g. A separate experiment proved that the retention due to kieselguhr was negligibly small.

RESULTS

The measurement of deuterium retention was carried out at temperatures between −200° and 350°C with 6.2 g of the nickel catalyst under 1 atm. Figure 2 shows typical chromatograms at different temperatures. The retention time is defined as the time lag of the deuterium peak relative to helium, as is usually done. From −150° to −70°C, the small helium peak was merged into the deuterium peak, the retention time for which

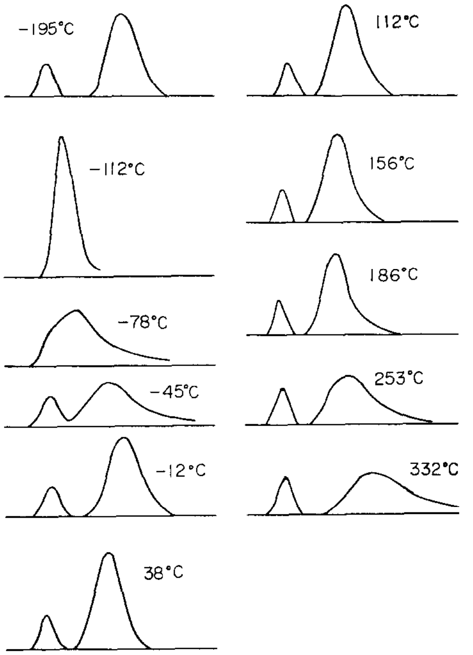

FIG. 2. Gas chromatograms of deuterium at different temperatures; first peak, helium.

TABLE 1
RETENTION VOLUMES OF DEUTERIUM

Reduction temperature: 350°C
Reduction time: 12 hr
Weight of catalyst: 6.2 g

Col. temp. (°C)	Ret. time (min)	Flow rate (ml/min)	Ret. volume [ml (STP)/ g cat.]
−195°	2.40	26.5	9.25
−145°	0.27	26.4	0.98
−112°	0.18	26.2	0.64
−78°	0.45	26.0	1.60
−56°	1.41	25.8	5.10
−45°	1.85	26.2	7.04
−28°	2.45	25.8	9.15
−12°	2.40	25.0	8.70
18°	2.20	25.2	8.05
38°	2.05	26.1	7.77
65°	2.00	25.2	7.33
113°	1.92	25.0	6.96
154°	1.75	26.8	6.80
186°	1.78	26.1	6.74
218°	1.94	25.6	7.19
253°	2.13	25.0	7.72
285°	2.33	24.7	8.35
318°	2.75	22.8	9.11
356°	3.25	21.8	10.25

was estimated from the respective apparent retention time which was measured separately. Thus the retention volume (STP) per gram of catalyst was obtained and is shown in Table 1 and in Fig. 3 as a plot against temperature. The plotted value is of course the one obtained after a stationary state was attained at each temperature and hence is independent of the direction of temperature variation.

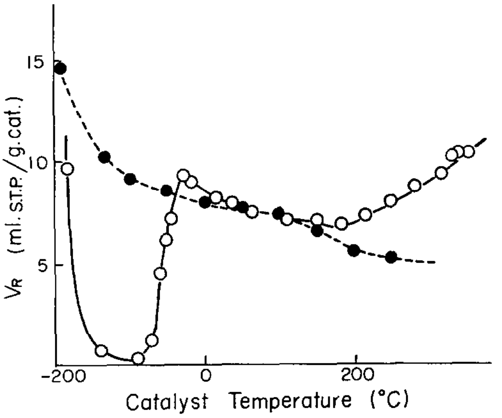

FIG. 3. Deuterium retention (open circle) and total uptake of hydrogen (filled circle) at different temperatures.

As may be seen in Fig. 3, the deuterium retention was appreciable at −195°C but diminished rapidly with rise in temperature to a negligible value at −100°C. It again increased at around −70°C and reached a maximum at −30°C. It may be said that there are two different temperature ranges in which the deuterium retention decreased with a rise in temperature, as follows: I, −195° to −100°C; and II, −30° to 180°C. In these ranges, the observed deuterium peak in the chromatogram was of symmetrical shape, while those observed in the range −70° to −30°C were tailed. In other words, when the column temperature was raised from the range I to II, a change in peak shape was observed as follows: First the tailing came out to the main symmetrical peak at around −70°C and then the height of the main peak decreased as the tail became significant. In the next place, the main peak and the tail were merged into a new peak of a larger retention time, although its shape was more broad. Further rise in temperature made it narrower.

The peak areas in ranges I and II were determined by half-width times peak height and proved to agree with each other with ±5% deviation, provided the sample size was constant. This common value of the peak area also agreed with that obtained when the pulse by-passed the catalyst column, as shown in Table 2. Thus the deuterium balance seemed to be satisfied.

TABLE 2
Relative Peak Areas[a]

Temp. (°C)	Relative peak area	Temp. (°C)	Relative peak area
−195	1.04	65	0.99
−112	0.96	97	1.01
−78	0.95	145	0.98
−56	0.76	197	0.95
−19	1.05	243	0.96
29	0.96	301	0.93
38	1.00		

[a] The peak area of the pulse which by-passed the catalyst column was taken as unity.

The composition of effluent pulse was 100% HD at any temperature. However when a smaller amount of catalyst, 2.1 g, was used, 40% of D_2 remained unreacted at −195°C, clearly showing the exchange to be slower than the adsorption process. Even in this case, the separation of HD from D_2 due to the isotope effect was hardly observed in the peak.

The total uptake of hydrogen by the catalyst under atmospheric pressure was measured volumetrically in a static system at decreasing temperatures after the catalyst was evacuated at 250°C for 2 hr. The amount of uptake is shown in Fig. 3 together with the retention volume of deuterium. The uptake increased monotonously with decrease in temperature, as is expected.

Discussion

1. *Implication of the Deuterium Retention*

It is generally accepted for ideal linear gas chromatography (*2*), where the concentration of sample gas in the adsorbed phase is proportional to that in the gas phase, that the distribution coefficient of the sample gas is obtained in terms of gas chromatographic retention volume as $\mu = V_R/V_0$, where V_R is the retention volume of sample gas due to the column material and is given as the difference between apparent retention volumes of the sample and a nonadsorbing gas such as helium, and V_0 is the net volume of carrier gas involved in the column.

An analogous quantity $\mu_D = V_{RD}/V_0$ for the deuterium retention can be defined, preserving the physical meaning of the distribution coefficient between adsorbed phase and gas phase, provided that the basic assumption of linear gas chromatography holds in the particular case, which can be confirmed by the symmetrical shape of the deuterium peak.

If a rapid adsorption equilibrium is established between the deuterium sample and the hydrogen adsorbed on the catalyst as the sample pulse proceeds along the column, and if the isotope effect in the adsorption is negligible, the deuterium concentration in the gas phase is equalized with that in the adsorbed phase, giving the relation

$$\mu_D = N_{aD}/N_{gD} = N_{aH}/N_{gH} = N_a/N_g \quad (1)$$

where $N_g = N_{gH} + N_{gD}$ (mole/g) is the amount of hydrogen involved in the gas phase of the column and $N_a = N_{aH} + N_{aD}$ (mole/g) is that in the adsorbed phase, which is in a rapid equilibrium with N_g. That is, N_a is the rapid and reversible part of the adsorbed hydrogen and hence not always in agreement with the total uptake of hydrogen by the catalyst. The subscripts H and D denote protium and deuterium, respectively.

Since both N_a and N_g are constant in a stationary state of the column, depending on temperature and pressure, N_a/N_g must be constant and unaffected by the introduction of pulse. This means that μ_D is constant at a given temperature and pressure, which is in accord with the treatment of linear gas chromatography. If the assumptions made above are valid in the present case, a symmetrical shape of the deuterium peak should result. This requirement was fulfilled in the temperature ranges −195° to −100°C and −30° to 180°C, as shown in Fig. 2, so that the value of $N_a = N_g\mu_D$ is determinable, whereas in the transition range between the above-mentioned ranges the apparent μ_D cannot be equalized with N_a/N_g because of the tailed peak.

It is to be noted that Eq. (1) is independent of the type of adsorption isotherm concerned, and that the only requirement for N_a is the constancy of N_a/N_g. Although the N_a/N_g must be a function of N_g, N_g was kept constant under the present experimental condition. Thus with any type of adsorption isotherm, if a rapid and reversible adsorption is taking place, the tracer gas introduced to the catalyst column should be retained for a while, depending the amount of adsorption concerned. This is the origin of the deuterium retention.

The amount of reversible adsorption N_a is now given by the equation

$$N_a = \mu_D N_g = (V_R/V_0)(PV_g/RT) \quad (2)$$

where $V_g = N_gRT/P$ (ml/g) is the gas space in the column per gram of catalyst, P is the ambient pressure of hydrogen, and T is the column temperature in °K. V_0 is given in terms of V_g and the catalyst weight W(g) as

$$V_0 = V_gWT_0/T \quad (3)$$

where T_0 is a standard temperature in °K.

Substituting (3) into (2),

$$N_a = V_RP/WRT_0 \quad (4)$$

or in a volumetric expression

$$V_a = N_aRT_0/P = V_R/W \text{ (ml/g)} \quad (5)$$

The quantity V_R/W plotted in Fig. 3 directly represents the amount of reversible adsorption, provided the basic requirement is fulfilled.

2. *Temperature Dependence of the Reversible Adsorption*

As already described, the variation of reversible adsorption (V_R/W) with temperature may be divided into two temperature ranges, I and II. In the intermediate range between them the observed peaks were tailed, with the retention volume increasing with temperature. The tailing is reasonably interpreted as indicative of the concurrence of slow adsorption–desorption. The slow activated adsorption appears to come out at around −70°C and to increase its rate with temperature up to −30°C, where the rate of adsorption and desorption is fast enough to establish equilibrium. This is reflected in the peak shape from which the tail disappears above −30°C.

In the two ranges I and II the reversible adsorption decreases with a rise in temperature as usually observed with isobar. In range II, particularly from 0°C to 150°C, the amount of reversible adsorption agrees with the total uptake, as seen in Fig. 2. This indicates full reversibility of the adsorbed hydrogen as measured as total uptake, that is, measured from the adsorption level retained after the evacuation at 250°C. The adsorbed hydrogen that is reversible above −30°C seems to be frozen below −100°C with negligible reversibility.

The reversible adsorption at −195°C amounts to two-thirds of the total uptake, a fairly high reversibility. If this adsorption is dissociative, the eluted pulse should not involve D_2 in addition to HD because the repetition of adsorption and desorption of deuterium in the carrier gas of hydrogen should result in equilibration of H_2–D_2 exchange. The presence of 40% D_2 in the pulse eluted from 2.1 g of catalyst column definitely indicates that the rapidly equilibrated adsorption at −195°C is undissociated. Thus the adsorbed state would be H_2 or H_2^+. The latter has been suggested by Suhrmann *et al.* on the basis of electric resistance measurement of evaporated nickel film. In any case, the heat of adsorption and the activation energy would be small and close to those of physical adsorption.

If at this temperature a dissociatively adsorbed and frozen hydrogen atom plays a role in the mechanism of deuterium exchange, as postulated in the Bonhöffer-Farkas or the Rideal mechanism, there must be delayed desorption of deuterium, which leads to either a tailed peak or lack of deuterium balance, because the rate of exchange is slower than that of reversible adsorption, as indicated by the incompleteness of exchange. Thus the observed symmetrical peak and preservation of deuterium balance at −195°C would suggest that the frozen hydrogen is inert in the exchange.

The whole feature of variation in the reversible adsorption so far discussed quite resembles that in the ordinary isobar of hydrogen (*4*) as measured by uptake at each temperature. This is reasonable on the ground of the activated adsorption concept (*5*). However, the reversible adsorption disagrees with the total uptake at higher temperature above 180°C, with discrepancy increasing with temperature. There must be more exchangeable hydrogen than the total uptake. Thus the exchangeable hydrogen left after the evacuation at 250°C was measured by isotope dilution, i.e., a measured amount of deuterium was circulated over the catalyst which was previously evacuated and was maintained at 250°C. After 1 hr of circulation, the gas composition was determined by mass spectrometry. The result gave 7.8 ml/g of hydrogen left on the catalyst, which is enough to explain the observed discrepancy. This suggests an exchange with tightly bound hydrogen which is nondesorbable with evacuation at 250°C. The bound hydrogen may include both adsorbed and dissolved hydrogen and that bound to kieselguhr (*6*), the catalyst support.

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