JOURNAL OF CATALYSIS 27, 215-221 (1972)

Hydrogen Chemisorption and Exchange on Platinum

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Received January 20, 1972

The pH_2, oD_2 and $H_2 + D_2$ reactions have been studied from 10^{-2} to 10 Torr and 77 to 500K, on a polycrystalline Pt wire cleaned in ultrahigh vacuum. Sticking coefficient studies have also been made from 5×10^{-8} to 5×10^{-5} Torr and 77 to 350K. Three temperature ranges are distinguished in terms of the following molecular mechanisms,

(a) 77–110K; $D_2 + MH \rightarrow MD + HD$
involving molecular adsorption on defect sites induced by the oxygen activation procedure. There is also a paramagnetic contribution to the spin isomerizations, since both oD_2 and pH_2 reactions go faster than $H_2 + D_2$

(b) 110–200K; similar to (a) but involving molecules in the whole van der Waals layer.

(c) >200K; $\frac{1}{2}H_2 + \frac{1}{2}D_2 + 2M \rightarrow MH\ MD \rightarrow 2M + HD$.

INTRODUCTION

Earlier work (*1, 2*) established platinum wire as a catalyst for the parahydrogen conversion and the activating effect of oxygen pretreatment. Later on (*3, 4*) evaporated films of platinum were used to demonstrate the exchange of molecular deuterium with chemisorbed H atoms on this metal, following up the first study on a film of tungsten (*5, 6*)

$$D_2 + HM \rightarrow MH + HD.$$

Work on platinum catalysts from our laboratory has concerned the absolute rate theory of the exchange mechanism (*7*), the pressure dependency (*8*) and activation energy of the conversion on wires (*9*), catalysis on films (*10*), and infrared studies of hydrogen adsorbed on supported platinum (*11*). There are problems concerning the effect of adsorbed oxygen on the activity of platinum (*1, 11, 12*) which require further study. In this paper we compare the rates of the pH_2, oD_2 and $H_2 + D_2$ reactions on a platinum wire using the methods used for nickel (*13*), and in addition obtain data on the sticking coefficient of hydrogen on platinum, but in a much lower pressure range than that of the catalytic studies.

EXPERIMENTAL METHODS

The catalysis system was the UHV apparatus used earlier for nickel (*13*). The cylindrical reaction vessel contained 12 cm of 42 SWG platinum wire (Johnson-Matthey Grade I) sealed down its axis, and was connected via two liquid nitrogen traps and a mercury cut off to the gas handling system. A length of 8 mm i.d. tubing connected the reaction vessel via a Metrosil leak to an A. E. I. MS10 mass spectrometer. The whole reaction system could be baked to 673K to give, after cooling, a residual pressure of 10^{-10} Torr. The pH_2 and oD_2 analyses were made by a micro-pirani gauge, and reactions were carried out over the pressure range 10^{-2} to 10 Torr and wire temperature 77 to 500K, the walls of the reaction vessel being maintained usually at 77K and the wire heated electrically, although in some individual experiments the whole reaction vessel was brought to the catalyst temperature [a necessary check to rule out the Busch effect (*13*)].

Sticking coefficients were studied over

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5×10^{-8} to 5×10^{-5} Torr in a conventional flow type UHV system. Hydrogen entered the system via PdAg thimble, then through a dekker valve into the cylindrical vessel containing axially a 16.5 cm Pt wire as above and then out via a second dekker valve, pumping port and liquid nitrogen trap. An Alpert gauge with a lanthanum hexaboride coated filament (to obviate dissociation of hydrogen) was directly adjacent to the adsorption wire. The dekker valves and pumping port were all magnetically operated. After bake-out and cooling the system held to 2×10^{-10} Torr. A furnace surrounding the PdAg thimble was used to control the rate of nflow of hydrogen.

RESULTS

Catalysis of pH_2, oD_2 *and* $H_2 + D_2$

Two procedures were used for filament activation, giving somewhat different results.

i Simple outgassing at $T > 1223$K, usually 1373–1423K for more than 60 min.

ii A cycle of treatments at 10^{-1} Torr oxygen at 1073–1173K, followed by reduction in 2 Torr hydrogen at 1273K and by outgassing at $T \leqslant 1073$K.

First order constants k_e are calculated from

$$k_e = \frac{1}{t} \ln \frac{x_0 - x_e}{x_t - x_e} \text{ min}^{-1}$$

where x_0, x_t and x_e are the fractions of pH_2 (or oD_2, or HD) at $t = 0$, t and equilibrium, respectively. This accurately accounts for the time-course of all three reactions.

The absolute rate as usual is

$$k_m = nk_e/60A \text{ molecules cm}^{-2} \text{ sec}^{-1}$$

where n is the number of molecules in the reaction vessel and A the area of the catalyst filament (taken as the geometric area). The apparent activation energy E and frequency factor B_m are given by

$$k_m = B_m \exp - (E/RT) \text{ molecules cm}^{-2} \text{ sec}^{-1}$$

and pressure dependencies by $k_m = k_m{}^0 p^a$.

The purpose of the oxygen pretreatment was to remove the possibility of any surface contamination of the platinum by atoms of carbon, and the pH_2 and oD_2 reactions were studied only on platinum wires so pretreated. So far as the $H_2 + D_2$ reaction is concerned we found a $\log_{10} k_m$(273K, 0.4 Torr) of 17.064 for simple outgassing method (i) and 17.646 for oxygen pretreatment method (ii), a small but reproducible effect. A simple flash desorption experiment established that a filament in state (ii) adsorbed approximately

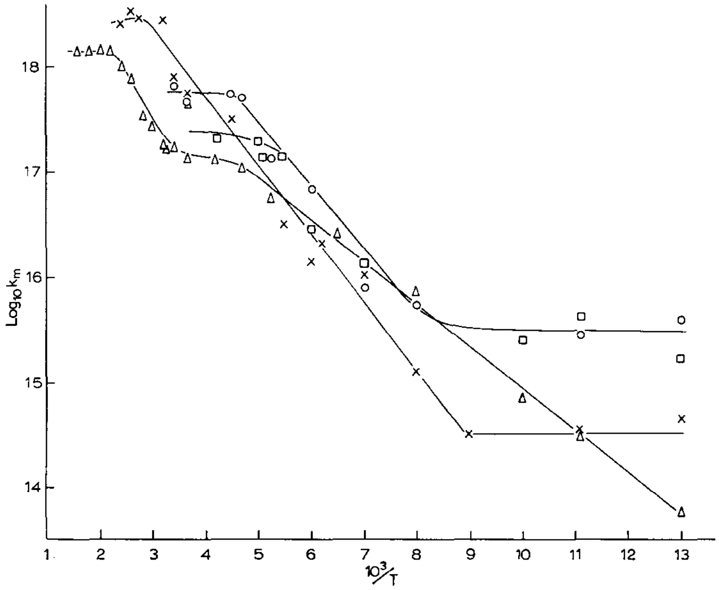

FIG. 1. Arrhenius plots for the Pt filament in state (i) (△) $H_2 + D_2$ (0.2–0.3 Torr); and state (ii) (○) pH_2 (0.5 Torr); (□) oD_2 (0.5 Torr); and (×) $H_2 + D_2$ (0.2–0.6 Torr).

one monolayer of hydrogen under our reaction conditions. In carrying out the complete series of reactions the cleanliness of the filament was checked between each series of runs by a standard run on $H_2 + D_2$ at 273K.

In summary, the $H_2 + D_2$ reaction was studied on the filament in state (i), and the $H_2 + D_2$, pH_2 and oD_2 reactions on the oxygen pretreated filament in state (ii). The temperature dependency data for $p = 0.2$ to 0.6 Torr are shown in Fig. 1, and the data are summarized in Table 1. This table also contains values of the external order a determined over 10^{-1} to 10 Torr, which at 273K all tend to zero at the highest pressure. In another series of experiments on $H_2 + D_2$ with the vessel walls at 177K, $a = 0.7 \pm 0.1$ for all five temperatures within a range 183–233K.

In addition, for purposes of discussion, in Table 1 we include calculated values of the collision number of H_2 (or D_2) molecules with the filament (per cm²).

$$Z = \frac{p}{(2\pi mkT)^{1/2}} \text{ molecules cm}^{-2}\text{ sec}^{-1}.$$

Sticking Coefficient of Hydrogen

After cleaning the Pt wire at 1073–1173K in a 2×10^{-10} Torr vacuum for 4 hr, essentially method (i), the walls of the adsorption vessel were cooled to 77K and the filament current was adjusted to give a filament temperature of 823K, at which no adsorption or molecular dissociation of hydrogen occurred. The hydrogen flow was then adjusted to give the working pressure, 5×10^{-8} Torr in the example shown in Fig. 2. Referring to this figure, when equilibrium flow had been reached, at zero time (point A) the filament current was switched off and hydrogen adsorption commenced. After allowing the appropriate adsorption time the two dekker valves were closed simultaneously and the filament flashed to 920K to desorb all the hydrogen (point B), i.e., Na molecules. The fractional coverage was then calculated on a basis of one hydrogen per site and $N_s = 1.4 \times 10^{15} A$ sites on the wire. The N_s calculation is based on an assumed roughness factor of unity, an effective wire length of 15.5 cm and area A 0.590 cm², and equal areas exposed of the two lowest energy, most close packed planes (111) and (110) of the fcc platinum filament, i.e., 1.4×10^{15} sites cm^{-2}. This assumption is consistent with that we made earlier for nickel (*14*). On this basis values of the fractional coverage $\theta = 2\text{Na}/N_s$ may be obtained as a function of time as in the example in Fig. 3, the possible error on the absolute value of θ being at least ±0.1.

TABLE 1

KINETIC DATA FOR Pt AT 0.2–0.6 TORR

Activation	T(K)	Parameter	pH_2	oD_2	$H_2 + D_2$
(i)	200–77	E	—	—	2.20
	200–77	$\log_{10} B_m$	—	—	19.4
(ii)	200–125	E	2.6	2.6	3.0
	200–125	$\log_{10} B_m$	20.3	20.3	19.4
	110–77	E	0	0	0
	110–77	$\log_{10} B_m$	15.5	15.5	14.5
	273	$\log_{10} k_m$	17.7	17.4	17.9 (17.1)
	77	$\log_{10} k_m$	15.5	15.5	14.5 (13.7)
	273	a	0.3–0.0	0.6–0.0	0.9–0.0
	77	a	—	0.2	—
		cf. data for Ni at 0.8–1.3 Torr			
—	273	$\log_{10} k_m$	17.32	16.85	17.12
—	77	$\log_{10} k_m$	16.00	15.90	13.00
		The Collision number Z at 0.4 Torr			
—	273	$\log_{10} Z$	20.78	20.63	
—	77	$\log_{10} Z$	21.05	20.90	

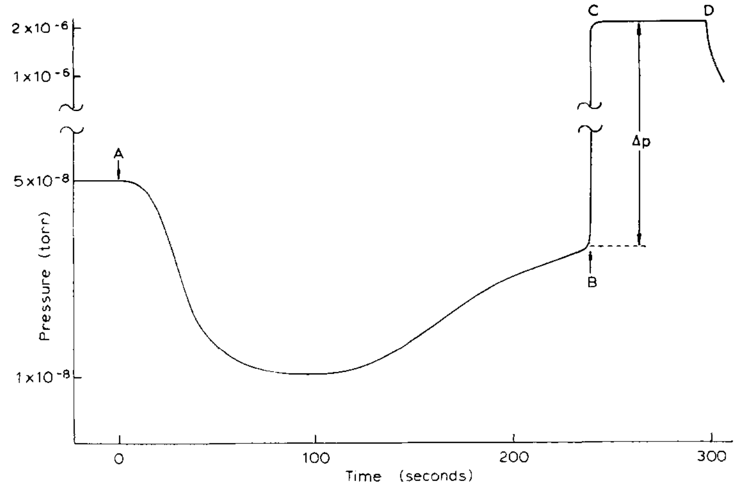

FIG. 2. A pressure-time plot for a flash desorption run at 5 × 10^{-8} Torr with the Pt filament at 77K.

By integration of the p/t profiles as in Fig. 2 it was possible to derive the integrated number of molecular collisions with the wire, N_{coll}, as a function of time, and hence to transform Fig. 3 into a plot of θ against N_{coll} (not shown here). From this plot we may derive the sticking coefficient S as a function of coverage

$$S = N_s(d\theta/dN_{\text{coll}}),$$

and results for various temperatures are plotted in Fig. 4. The sticking coefficient as determined here refers to the net difference between adsorption and desorption rates, and this must be remembered in considering the falloff in S with increase in θ and T.

The effect of oxygen pretreatment of the filament is indicated in Fig. 3. In this case the filament was exposed at 1173K to 3 Torr oxygen for 10 min, followed by pumping and reduction at 1073K in 5 × 10^{-6} Torr of flowing hydrogen for 2 hr. A similar result was obtained if the reduction process was carried out at 1273K in 3 Torr of flowing hydrogen for 2 hr. The oxygen pretreatment has apparently had little effect on the roughness factor.

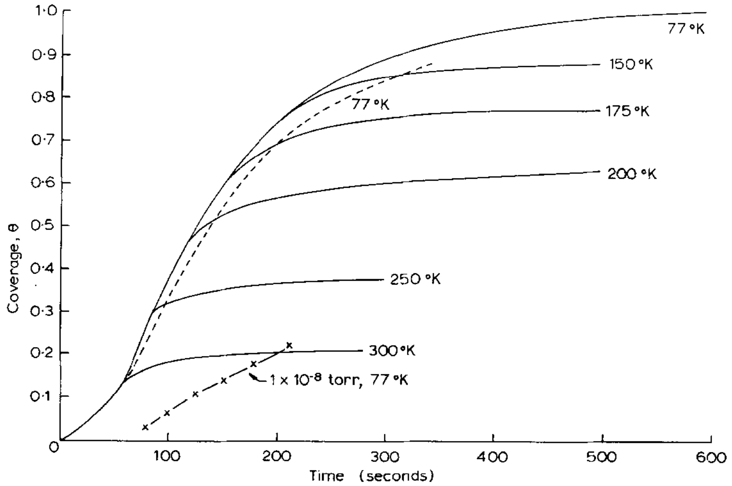

FIG. 3. Fractional coverage θ as a function of time, at 5 × 10^{-8} Torr and for various filament temperatures. (- -) a filament at 77K after oxygen pretreatment. A run at 77K and 1 × 10^{-8} Torr is indicated.

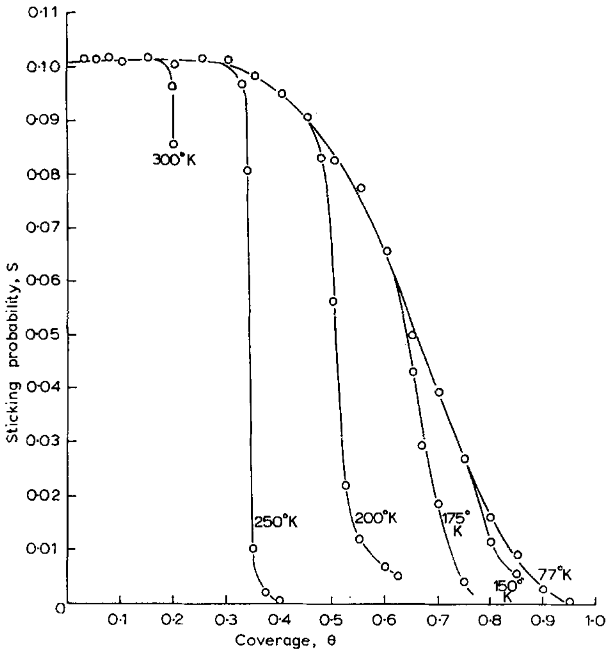

Fig. 4. Sticking coefficient S as a function of coverage θ at various temperatures.

DISCUSSION

As in our paper on nickel (*13*), we consider our results in terms of the Lennard-Jones potential curves for hydrogen on a metal, as modified by Dowden to include Type C chemisorption (molecular), cf. Fig. 5. The mechanisms considered are numbered as previously (*13*)

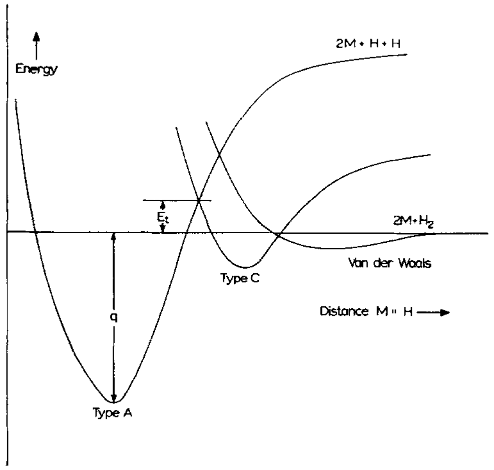

Fig. 5. Potential energy curves for Type A(2M-H) and Type C (M · · · H_2) chemisorbed hydrogen. E_t is the activation energy for chemisorption and q the heat of chemisorption.

$$pH_2(\text{or } oD_2) + P \rightarrow P + oH_2(\text{or } pD_2) \quad \text{(I)}$$

P is a paramagnetic site. This does not equilibrate $H_2 + D_2$

$$pH_2 + M\cdot M \rightarrow MHMH \rightarrow M\cdot M + oH_2 \quad \text{(II)}$$

$$pH_2 + M\cdot MH \rightarrow MH_2MH \rightarrow MHM + oH_2 \quad \text{(IIIa)}$$

$$pH_2 + MH \rightarrow MH_3 \rightarrow MH + oH_2 \quad \text{(IIIb)}$$

Mechanisms II, IIIa and IIIb also, of course, catalyze $oD_2 \rightarrow pD_2$ and $H_2 + D_2 \rightarrow 2HD$.

From the sticking coefficient work in Fig. 3, at 5×10^{-8} Torr, it seems fairly certain that in the catalytic studies at $p = 0.1$–10 Torr, that for $T < 200$K we should expect $\theta \geq 1.0$ ($\theta > 1.0$ corresponds to a full atomic layer *plus* molecular adsorption, probably Type C chemisorption). From the sticking coefficient results in Fig. 4 it is apparent that for hydrogen molecules striking a platinum surface $0 < \theta < 0.35$, that the activation energy for chemisorption, E_t in Fig. 5, is effectively zero. We shall assume that this is effectively true for higher coverages, as desorption effects complicate the further analysis of higher coverages in Fig. 4.

We now turn to the catalytic results of Fig. 1 and Table 1, and the Arrhenius plots can be divided into three ranges of temperature separated by discontinuities.

a. 77–110K: The effect of oxygen pretreatment is to introduce a discontinuity into the Arrhenius graph for $H_2 + D_2$, not present for the annealed surface. We are, therefore, led to postulate a mechanism

$$pH_2 + M{\cdot}MH \rightarrow MH_2MH \rightarrow MHM + oH_2 \qquad \text{IIIa}$$

for all three reactions, pH_2, oD_2 and $H_2 + D_2$ with an activation energy of zero. The MH sites will have $\theta \geq 1.0$ and the empty M sites will be defect sites, generated by oxygen treatment and removable by annealing, which adsorb molecular hydrogen. This is therefore a Rideal mechanism (*14*) but occurring on a very few defect sites which corresponds to the low frequency factor found $B_m \ll Z$. Alone, this mechanism should give a rate order $pH_2 > H_2 + D_2 > oD_2$ and since we observe $pH_2 = oD_2 > H_2 + D_2$ it is necessary to postulate a paramagnetic contribution to the rate, mechanism I [see Ref. (*13*) for a full discussion]. Since Pt atoms are paramagnetic in the metal, this may be expected as for Ni (*13*). For nickel filaments the ratio of the rates of the parahydrogen conversion and hydrogen deuterium exchange is $\sim 10^3$, while for a nickel film the ratio is only about 10, so this is more analogous to the oxygen pretreated Pt wire.

b. 110–200K: Over this range the Pt wire [state (i)] shows an $H_2 + D_2$ activation energy $E = 2.2$ kcal mole^{-1}, and in state (ii), $E = 3.0$ kcal mole^{-1} and for pH_2 and oD_2 $E = 2.6$ kcal mole^{-1}. Since we expect the Pt surface to be completely covered with chemisorbed H, $\theta \simeq 1.0$, it seems probable that mechanism IIIb is operative.

$$pH_2 + MH \rightarrow MH_3 \rightarrow MH + oH_2$$

where the hydrogen molecules are adsorbed in the van der Waals layer over the whole surface (*7*), possibly in the precursor state revealed in sticking coefficient work (*15*). The frequency factor for the reaction involving a dilute van der Waals layer should approximate to the simple collision number, $B_m \simeq Z$, as found in Table 1. An external order of 0.7 would, in fact, correspond roughly to a molecular coverage of 0.3, if the atomic hydrogen layer was complete. The present k_m (pH_2) values compare closely with those determined by Couper *et al.* (*9*) over 130–180K of $E = 2.7$ kcal mole^{-1} and $\log_{10} B_m$ (1.2 Torr) $= 21.32$, which corrects to our pressure as $\log_{10} B_m$ (0.4 Torr) $= 20.84$, compared with $E = 2.6$ kcal mole^{-1} and $\log_{10} B_m = 20.3$.

It is apparent that the oxygen pretreatment has changed the $H_2 + D_2$ Arrhenius plot over the whole of this range which suggests that the influence of the defect sites, whatever their origin, spreads over the whole surface. The effect, however, on the flash filament seen at 77K in Fig. 3 is small.

c. $T > 200$K: It is clear from Fig. 1 (but not listed in Table 1) that all reactions at a certain temperature, which varies from one reaction to the next, go through a discontinuity to give $E = 0$. Clearly at some stage, we expect the onset of hydrogen atom desorption as molecules to become important (at the abrupt drop in S at 200K for $\theta = 0.5$ for the molecular pressure of 5×10^{-8} Torr in Fig. 4). In these circumstances mechanism II will become rate determining. At high coverage the heat of adsorption will probably fall to a very low value [e.g. Ref. (*14*)] and E_t is assumed to remain $\simeq 0$. Under these circumstances the activation energy for desorption would be ≈ 0 in keeping with the observed activation energy. The discontinuity may be pictured in the following way. In the temperature range 100–200K the catalytic exchange is governed by mechanism IIIb as described. As the temperature is raised two effects will be important; (i) depopulation of the loosely held "molecular layer" and (ii) increasing mobility in the atomically bound hydrogen layer. If desorption is rate determining then a true sticking coefficient of $\sim 10^{-3}$ is required. If on the other hand the true sticking coefficient remains constant to very high coverage the rate-limiting step must be exchange in the atomically held layer and the activation energy would be characteristic of a diffusion process, which would be expected to be very low at high coverage (*16*). It is impossible to decide between these two choices on the basis of the present work.

The main weakness in the present paper concerns a comparison of reaction velocity measurements, with adsorption studies at a much lower pressure. In future work, we hope the measurements may be made on the identical wire for the identical pressure range.

ACKNOWLEDGMENTS

The authors thanks are due to the SRC for equipment, and a studentship for P.R.N., and to I.C.I. Ltd. for a fellowship for R.J.B.

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