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Inhibition of Hydrogen Desorption from a Thin Palladium Layer by Surface Poisoning

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The effect of preadsorbed CS_2 molecules on the desorption kinetics of hydrogen from a thin Pd layer is reported. The studies have been carried out with a piezoelectric quartz crystal mocrobalance in the α-phase region on a Pd layer of 3000 Å thickness at 59.6°C and at different degrees of poisoning, namely, $\theta_{CS_2} = 0, 0.2$, and 0.8. The two stages by which H_2 is removed from Pd are influenced by CS_2 molecules, i.e., the transfer–recombination stage (for dissolved H atoms) and the surface migration–recombination stage (for strongly bound H atoms). The effect of the poison lies in the apparent decrease of the permeation surface, where the weakly bound H atoms are located, affecting not their areal density but rather their surface mobility. The change of the desorption and absorption rate constants with the degree of poisoning exhibits a behavior resembling a catalyst poisoning curve.

INTRODUCTION

The sorption of hydrogen in a thin layer of palladium occurs by a composite mechanism which involves different kinds of adsorbed hydrogen (*1–3*). The presence of these distinct kinds of hydrogen atoms in the interface region is due to the heterogeneity of the palladium surface (*3, 4*), and has important implications for its catalytic activity (*5*). The degree of participation of the adsorbed hydrogen species in a catalytic reaction depends, besides the nature of the reactants, on their interaction energy with the corresponding adsorption sites.

In order to identify the reactive adsorbed H atoms present in the interface region of the α phase of a (Pd–H) sample and its relationship with the dissolved hydrogen, we have studied the effect of CS_2 poisoning on the rate of desorption of hydrogen from a thin palladium layer (*2*) using a piezoelectric quartz crystal microbalance (PQCMB) (*1–3, 6*).

It is well known that the adsorption of poisoning molecules on a catalytic surface inhibits activity due to the blockage of the active sites (*7, 8*). In the case where hydrogen is involved, these adsorption sites supply the relatively mobile (weakly bound) H atoms, which participate in the catalytic reaction. The poisoning of the surface causes a decrease in the coverage of these mobile H atoms.

The desorption of hydrogen from palladium involves the same mobile H atoms; and, consequently, any change of the desorption rate should correlate with the change of the catalytic activity of the palladium surface. A similar effect has been found by Maxted and Evans in studying a Pt black catalyst (*9*).

The poison used in this study was carbon disulphide because it best suited our working conditions: CS_2 is strongly adsorbed on the palladium surface (*3*), does not react with hydrogen or carrier gas, can be readily removed by oxidation, and has a low limit of detectability with the PQCMB technique (*3, 6*). Carbon disulphide has been recently used successfully in the poisoning titration technique on supported platinum catalyst (*10*).

EXPERIMENTAL

The experiments have been carried out in the α phase region of the (Pd–H) system at constant temperature (59.6°C) with the

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PQCMB technique described in detail elsewhere (1–3, 6). The quartz plate was coated on both sides with a thin paladium layer of about 3000 Å thickness and 0.8 cm^2 geometrical surface area. The metallic layers have been obtained by vacuum evaporation of high-purity palladium (Specpure, Johnson & Matthey, Ltd.). The nominal frequency of the quartz crystal plate was $f_q^0 = 5.023$ MHz and its weight sensitivity $\sigma = 2 \times 10^8$ Hz/g.

The sample has been treated adequately in order to obtain a relatively clean surface and to stabilize the bulk structure of the metallic layer: the sample was treated in a stream of He at 110°C until no change in the frequency was observed (10 h), followed by 10 repeated absorption–desorption cycles with hydrogen at the same temperature (1–3). Furthermore, the temperature was changed at 59.6°C and the thin palladium layer was charged with hydrogen by equilibration with a given partial pressure of H_2 in a H_2 + He mixture, corresponding to the linear part of the calibration curve (3). The absorption of hydrogen in the thin palladium layer was followed by the change in the frequency shift of the PQCMB until it reached a constant value. This value is ascribed to the equilibrium state.

The desorption was initiated by stopping the inlet of hydrogen in the He carrier gas. As a result, the frequency shift changes in the reverse direction due to the decrease of the mass of the palladium layer by the removal of the previously adsorbed hydrogen. The frequency-shift–time curves were recorded and then used to estimate the kinetic parameters. This procedure was used in the experiments both with the uncontaminated surface (designated Sample 1) and with the poisoned palladium surface.

The poisoning of the sample was accomplished by adsorption of CS_2. The sample was removed from the PQCMB cell and was exposed to argon saturated with CS_2 vapour at room temperature, for 5 min. Afterwards it was introduced again in the PQCMB cell and a frequency shift $\Delta F_{CS_2}^{eq} = 4.64$ Hz was measured, corresponding to 1.84×10^{14} molecules of adsorbed CS_2 or 3.7×10^{14} adsorption sites. This value involves a factor of two for the adsorption stoichiometry (10). The equilibrium adsorption of O_2 on the uncontaminated surface gave a frequency shift of $\Delta F_0^{eq} = 2.5$ Hz, corresponding to a total number of adsorption sites of 4.7×10^{14} (3). The corresponding coverage with CS_2 was estimated at $\theta_{CS_2} = 0.8$ (Sample 2). Furthermore, by treatment of the sample with oxygen at 59.6°C for 20 h, CS_2 was partially removed from the palladium surface. Repeating the equilibrium adsorption of O_2, we then found $\Delta F_0^{eq} = 2.0$ Hz, which corresponds to 3.7×10^{14} adsorption sites, and hence $\theta_{CS_2} = 0.2$ (Sample 3).

The effect of surface poisoning on the desorption kinetics of hydrogen is reflected in the frequency-shift–time curves shown in Fig. 1, where the ordinate represents the relative change of the frequency shift referred to the steady-state value $\Delta F_d^{eq} = 7.96$ Hz ($r = \Delta F_d / \Delta F_d^{eq}$). The curves have been recorded starting from the same initial concentration of hydrogen dissolved in the palladium layer, $N_i^{eq} = 11.6 \times 10^{-4}$ g-atom/cm^3 (equilibrium pressure $p_{H_2}^{eq} = 21$ Torr). The rate of desorption is strongly affected by CS_2: a decrease of 50% in the r values is reached in about 160 s (Sample 1), 380 s (Sample 2), and 690 s (Sample 3), respectively. It must be emphasized that the shape of the curves also changes; this is particularly obvious for Samples 1 and 2.

While the desorption process is strongly affected by poisoning the surface, the calibration curve is not influenced at all. In Fig. 2 the steady-state values of ΔF_d^{eq} are plotted versus the equilibrium (initial) concentration of hydrogen held within the thin palladium layer, N_i^{eq}, for all three samples. The experimental points fit very well the same straight line described by the relationship $\Delta F_d^{eq} = 2.67 + 4590\, N_i^{eq}$ (for $N_i^{eq} > 8 \times 10^{-4}$ g-atom/cm^3). It follows that in spite of the fact that even 80% of the total number of weak adsorption sites are

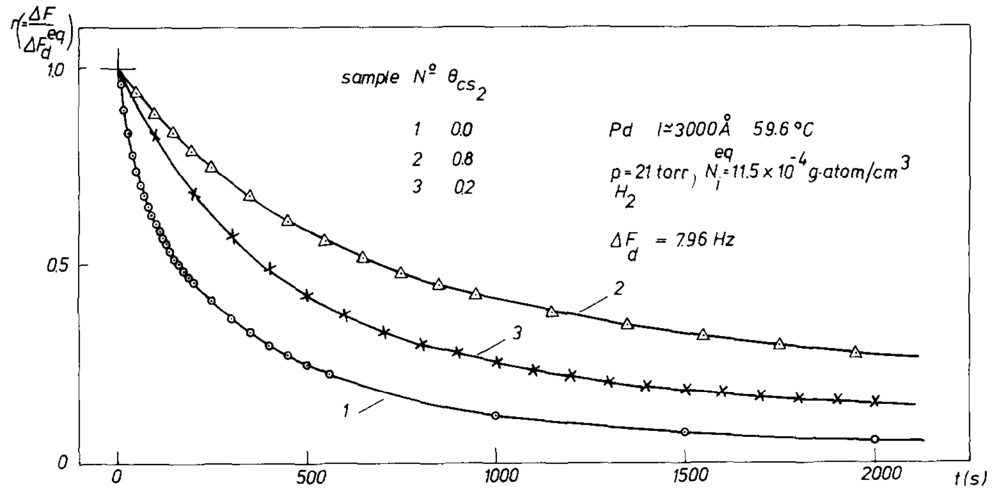

FIG. 1. Effect of the degree of poisoning θ_{CS_2} on the relative change of the frequency shift during the desorption process.

blocked by CS_2 molecules, the remaining free adsorption sites are ample to accommodate the equilibrium concentrations of the weakly and strongly bound H atoms.

DISCUSSIONS

The desorption of hydrogen located in and on the thin palladium layer occurs by the mechanism shown in Fig. 3, where H_i is the hydrogen dissolved in the thin palladium layer (volume V), H_w is weakly adsorbed hydrogen on the permeation surface S_w, H_s is the strongly adsorbed hydrogen on the adsorption surface S_s, and $H_2(g)$ is the gaseous hydrogen (*3*, *4*). The first stage of desorption is the following: the hydrogen atoms H_i move from the dissolved state in the metal lattice towards the weak adsorption state by the transfer step 2. This step, which corresponds to a fast dynamic equilibrium, is followed by the recombination of the weakly bound H atoms to molecules and further by their removal from the permeation surface, step 1. The recombination

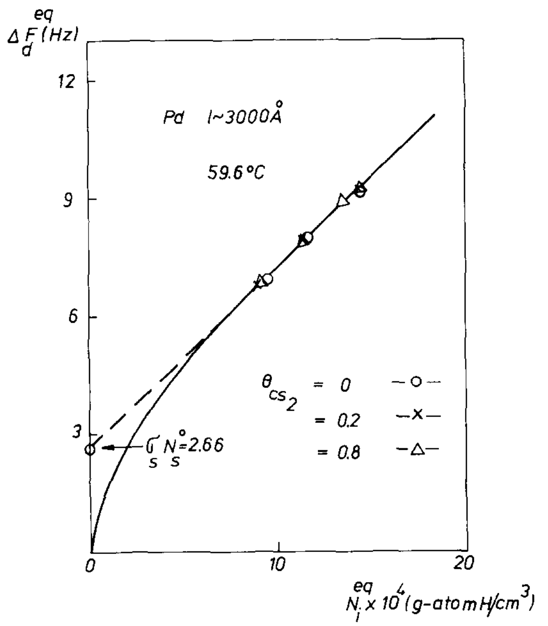

FIG. 2. Calibration curves of the piezoelectric quartz crystal microbalance for the three different samples.

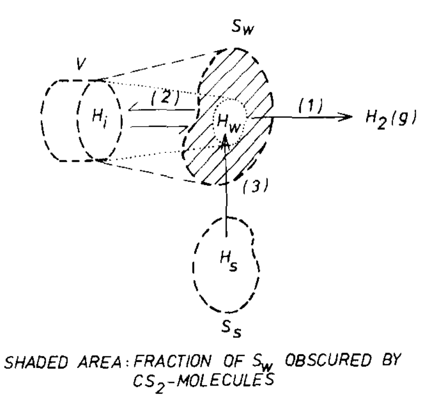

FIG. 3. Mechanism of hydrogen desorption from a thin palladium layer. Shaded area: Fraction of S_w obscured by CS_2 molecules.

can occur in two ways: (a) *the weakly bound H atoms* walk randomly on the permeation surface until pairs simultaneously reach two adjacent sites suitable for attractive interaction and thereafter for the formation of H_2 molecules; (b) *the dissolved H atoms* simultaneously reach two adjacent sites on the permeation surface, interact together and then are removed as H_2 molecules.

After the first stage has advanced sufficiently, the removal of the strongly adsorbed hydrogen starts under the kinetic control of the surface migration, step 3. As has been discussed elsewhere (*3*, *4*), this step is slower than the recombination and becomes singly operative in the overall desorption rate only in the very last period. In the intermediate period the two stages overlap and operate together. The rate determining character of the surface migration is due to its activation energy being larger than the recombination step (*3*). The desorption rate of the dissolved hydrogen v_d during the first stage is given by Eq. (1) (*3*, *4*)

$$v_d = k_d N_i^2, \qquad (1)$$

where N_i is the concentration of dissolved hydrogen atoms (g-atom/cm³) and k_d is the formal rate constant (cm³/g-atom · s),

$$k_d = 2k_{-1}S_w/[(K_2V + S_w)K_2]. \qquad (2)$$

Here k_{-1} is the true desorption rate constant of the weakly bound hydrogen (cm²/g-atom · s) and K_2 is the equilibrium constant for step 2 (cm^{-1}). Since $K_2V \gg S_w$ (*3*), Eq. (2) simplifies and becomes

$$k_d \simeq 2k_{-1}\frac{S_w}{K_2^2V}. \qquad (2')$$

The desorption rates have been calculated by converting the changes of frequency shift into the corresponding changes of concentration using the calibration curve (Fig. 2), followed by differentiation with respect to time. The results are shown in Fig. 4, according to Eq. (1), and correspond to the data given in Fig. 1. It can be seen that the initial period of the desorption process (N_i decreases from N_i^{eq} to zero) obeys Eq. (1) quite well, and also that the domain of second-order kinetics increases with the degree of poisoning of the palladium surface.

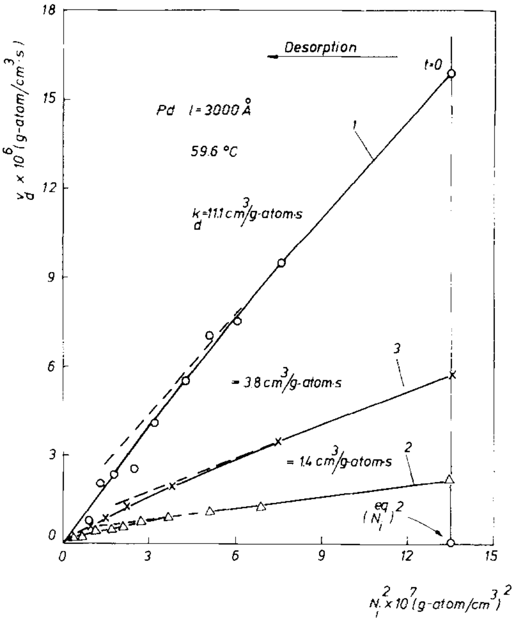

FIG. 4. Effect of the degree of poisoning θ_{CS_2} on the desorption rate v_d; the initial dissolved concentration of hydrogen N_i^{eq} = 11.5 × 10^{-4} g-atom/cm³ at t = 0.

The slope of the linear parts of the v_d curves enables us to estimate the k_d values and these are given in Table 1.

The values of the formal rate constants k_d can also be estimated from the r values by the kinetic analysis developed previously (*11*). The relationship valid for the second-order kinetic control of the desorption process is

$$\frac{1 - r}{r - \epsilon_d^{II}} = k_d^{II}t, \qquad (3)$$

where ϵ_d^{II} is a correction factor and k_d^{II} is the experimental rate constant

$$k^{II} = 2k\frac{S_w}{(K_2V + S_w)K_2}N_i^{eq}$$

$$\simeq 2k_{-1}\frac{S_w}{K_2^2V}N_i^{eq}. \qquad (4)$$

TABLE 1

Dependence of Second-Order Rate Constant of H Desorption on the Degree of Coverage of Pd Surface with CS_2; 59.6°C, $p_{H_2}^{eq} = 21$ Torr

Sample	θ_{CS_2}	k_d^{II} (s^{-1})	$N_i^{eq} \times 10^4$ (g-atom/cm^3)	$k_d(=k_d^{II}/N_i^{eq})$ (cm^3/g-atom · s)	$k_d(=v_d/N_i^2)$ (cm^3/g-atom · s)
1	0	1.56×10^{-2}	11.64	13.4	11.1
2	0.8	1.63×10^{-3}	11.51	1.4	1.4
3	0.2	3.63×10^{-3}	11.51	3.2	3.8

Note. θ_{CS_2} = degree of coverage with CS_2; k_d^{II}: experimental second-order rate constant; k_d: formal second-order rate constant; v_d: desorption rate.

It is obvious that $k_d = k_d^{II}/N_i^{eq}$.

The plot of the experimental data from Fig. 1 according to Eq. (3) is shown in Fig. 5a and the corresponding kinetic parameters are also given in Table 1. The domain of second-order kinetics in Fig. 5a also increases appreciably with the degree of poisoning of the palladium surface: for Sample 1 it is less than 100 s, while for Samples 2 and 3, it is larger than 2000 s. In this respect the effect of poisoning is similar to that due to the changes of permeation surface area previously reported (*2*). This suggests that the diminution of the desorption rate by CS_2 poisoning can be chiefly connected with the decrease of the permeation surface area.

The formal second-order rate constants k_d are considerably affected by poisoning the palladium surface. Their values are given in Table 1 and are quite identical regardless of the method used for their calculation. This agreement besides the validity of the mechanism proposed for the first stage of sorption (*3*, *4*), also supports the approaches involved in the kinetic analysis of *r* curves (*11*). Further we shall use just this calculation method in order to study systematically the effect of poison on the desorption rate.

The rate determining step in the last stage of desorption is the surface migration and therefore the *r* curves obey a first-order kinetic relationship:

$$\ln r = \text{const} - k_d^I t, \qquad (5)$$

with

$$k_d^I = (S_W/S_S)k_{-3}, \qquad (6)$$

where k_d^I is the experimental first-order rate constant and k_{-3} is the true backward surface migration rate constant (s^{-1}) (*3*, *4*). The semilog plot according to Eq. (5) is given in Fig. 5b: the poisoning of the palladium surface increases the first-order kinetic domain, but diminishes by about one order of magnitude the k_d^I value at $\theta_{CS_2} = 0.8$.

The influence of poisoning on the desorption rate of hydrogen from a thin palladium layer is summarized in Table 2. Whereas Samples 1, 2, and 3 have a well-defined degree of poisoning, Samples 4 and 5 have not, but they are characterized by the kinetic parameters.

In accordance with the theoretical analysis (*3*, *4*), the desorption rate constants k_d and k_d^I do not depend on the initial (equilibrium) hydrogen concentration N_i^{eq}, but are simultaneously affected by surface poisoning (Sample 2) or by the decontamination treatment applied later (Samples 3, 4, and 5). The prolonged oxidation in oxygen atmosphere at 59.6°C does not restore the initial desorption rate (sample 4); an advanced but still incomplete recovery of the initial surface properties can be achieved by cleaning with a commercial emulsion of surface active agents (3%v/v "Decon"-solution[1]) (sample 5). However, a pro-

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[1] Obtained by the kindness of Decon Laboratories Ltd., England.

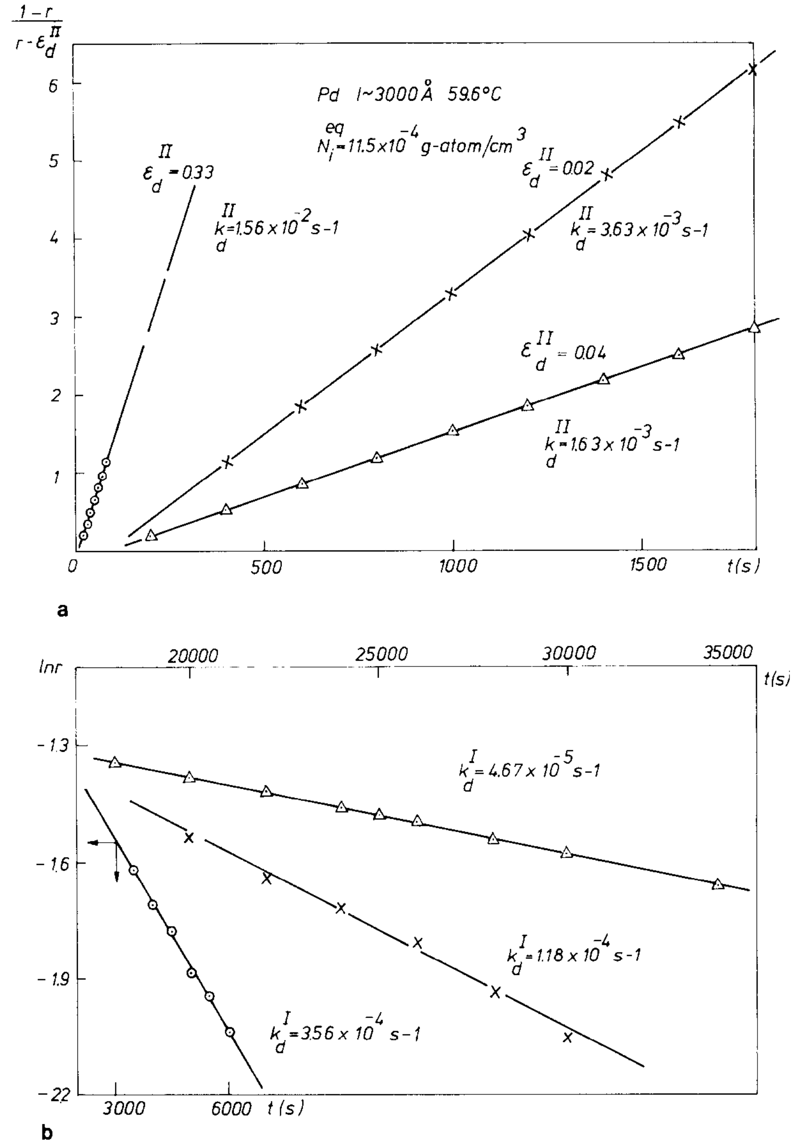

FIG. 5. Kinetic analysis of the experimental data shown in Fig. 1: (a) second-order kinetic control; (b) first-order kinetic control.

longed contact of the sample with hot "Decon" solution (during 2 h) causes irreversible changes of the surface structure of the palladium layer probably due to a slight corrosion.

The last two columns Table 2 must be discussed in detail: the product $\epsilon_d^{II} \times \Delta F_d^{eq}$ represents the frequency shift due to the desorption of the fraction of the strongly adsorbed hydrogen by the first-order kinetics alone, i.e., without the superposition of the second-order kinetics (*11*); the $\sigma_s N_s^0$ value is the frequency shift corresponding to the overall desorption of hydrogen which saturates at equilibrium the strong adsorption sites and it is estimated from the intercept of the calibration curves (Fig. 2). For a clean palladium surface (Sample 1), where the desorption rate is quite fast, these two values are practically the same, as theory

TABLE 2

Effect of Poisoning with CS_2 on the Kinetic Parameters of H Desorption from a Thin Pd Layer, l = 3000 Å, 59.6°C

Sample No.	Pretreatment	θ_{CS_2}	$N_i^{eq} \times 10^4$ (g-atom/cm^3)	ΔF_d^{eq} (Hz)	ϵ_d^{II}	k_d^{II} (s^{-1})	k_d (cm^3/g-atom · s)	$k_d^I \times 10^4$ (s^{-1})	$\epsilon_d^{II} \times \Delta F_d^{eq}$ (Hz)	$\sigma_s N_s^0$ (Hz)
1	20 h at 110°C in He (1 atm)	0	14.36	9.16	0.27	0.0178	12.4	5.5	2.50	
	20 h at 59.6°C in O_2 (1 atm)		11.64	7.97	0.33	0.0156	13.4	3.6	2.63	
	O_2 adsorption: ΔF_O^{eq} = 2.5 Hz		9.47	6.90	0.34	0.0106	11.2	5.5	2.35	
	n_O = 4.7 × 10^{14} sites		14.36	9.25	0.28	0.0170	11.9	4.3	2.59	
					Av. values:		12.2	4.7	2.52	2.48
2	5 min at 23°C in Ar saturated with CS_2	0.8	13.54	8.92	0.06	0.0020	1.49	—	0.54	
	CS_2 adsorption: ΔF_{CS_2} = 4.64 Hz		11.51	7.95	0.04	0.0017	1.43	0.5	0.32	
	n_{CS_2} = 3.7 × 10^{14} sites		9.14	6.89	0.046	0.0014	1.48	0.6	0.32	
			14.36	9.27	0.025	0.0022	1.50	0.7	0.23	
					Av. values:		1.48	0.6	0.35	2.69
3	20 h at 59.6°C in O_2 (1 atm)	0.2	14.29	9.26	0.02	0.0043	3.0	1.1	0.19	
	O_2 adsorption: ΔF_O^{eq} = 2.0 Hz		11.51	7.95	0.02	0.0036	3.2	1.2	0.16	
	n_O = 3.7 × 10^{14} sites		9.03	6.86	0.01	0.0032	3.6	2.0	0.07	
					Av. values:		3.3	1.4	0.14	2.84
4	20 h at 75°C in He (1 atm)	—	13.37	8.63	0.015	0.0038	2.8	1.2	0.13	
	36 h at 59.6°C in O_2 (1 atm)		14.00	9.13	0.02	0.0051	3.6	—	—	
					Av. values:		3.2	1.2	0.13	
5	15 min at 90°C in 3% v/v "Decon" solution 13 h in H_2 ($p_{H_2}^{eq}$ = 21 Torr)	—	14.1	8.75	0.2	0.012	8.4	2.6	1.74	—

predicts (*11*). On the contrary, on a poisoned surface, the removal of dissolved hydrogen (second-order process) is much delayed and most of the strongly adsorbed hydrogen is removed together with it. Consequently the quantity of the strongly bound hydrogen which is desorbed by a first-order process alone diminishes and so does the $\epsilon_d^{II} \times \Delta F_d^{eq}$ value.

It is noteworthy that whatever the degree of poisoning of the palladium surface, the poison acts in the same proportion on both rate constants k_d and k_d^1. This is obvious from Fig. 6, where the second-order rate constant, k_d, is plotted against the first-order rate constant k_d^1; the figures correspond to the samples from Table 2. The linear relationship shown in Fig. 6 suggests that the poison affects a common parameter which is involved in both the second- and first-order kinetic process, that is, the permeation surface area, S_w. In fact, both rate constants depend proportionally on the magnitude of S_w, Eq. (2′) and Eq. (6), and it seems as if the adsorption of CS_2 molecules diminishes the S_w value without affecting the amount of the adsorption sites N_w^0 available to accommodate the weakly bound hydrogen, i.e., the areal density (coverage) of H_w atoms. In accordance with Fig. 3, the removal of either the dissolved hydrogen (H_i) or the strongly adsorbed hydrogen (H_s) occurs through the weakly adsorbed hydrogen (H_w) located on the permeation surface. Hence any change in its magnitude will cause changes in the rate of any of the stages involved in the desorption process.

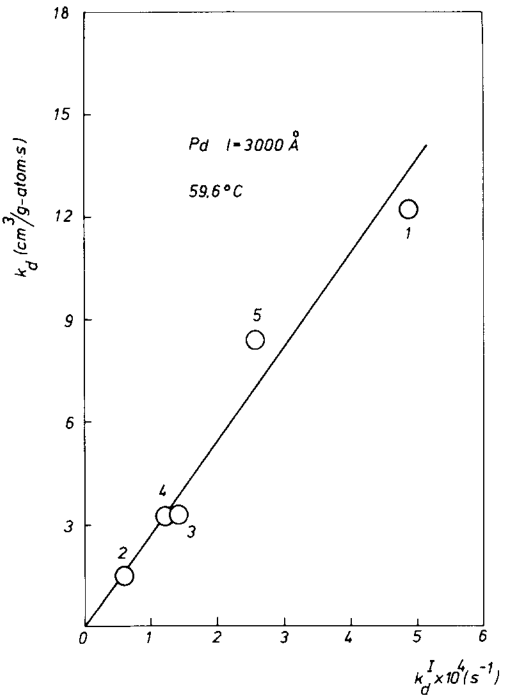

FIG. 6. Plot of the second-order rate constant k_d against the first-order rate constant k_d^1 for the desorption process.

The apparent decrease of the permeation surface area due to the adsorption of the CS_2 molecules is not well understood. Briefly, two suppositions can be discussed:

(a) The adsorption sites for the CS_2 molecules are different from those specific for the weak hydrogen adsorption. In this case the poisoning effect simply consists of the screening of the hydrogen adsorption sites.

(b) The adsorption of the CS_2 molecules occurs on the same weak hydrogen adsorption sites, but their influence spreads over a larger number of sites than those effectively blocked by the poison. Therefore the fraction of the permeation surface area affected by the CS_2 molecules is larger than the effective surface area occupied by these molecules.

This last supposition can be quantitatively argued as well, taking into account the equilibrium areal density of the weakly bound H_w atoms, N_w^{eq}. In our experiments it was: $N_w^{eq} = 10^{-11}$ g-atom H/cm^2 for $N_i^{eq} \cong 10^{-3}$ g-atom H/cm^3, and $K_2 = 10^8$ cm^{-1} (*3*); i.e., it corresponds to $n_w^H = 6 \times 10^{12}$ sites/cm^2 occupied by the weakly bound H atoms. On the other hand, the available free adsorption sites on the poisoned surface with $\theta_{CS_2} = 0.8$ is $n_w = 1.2 \times 10^{15} \times 0.2 = 2.4 \times 10^{14}$ sites/cm^2, which offers enough room for the H_w atoms to move freely over the permeation surface. Hence one has to accept that the adsorbed CS_2 molecules do not affect *directly* the areal density of the H_w atoms, but rather their mobility by a long-range effect. Unfortunately the information in the literature concerning the interaction of CS_2 with the metallic surface is scarce (*12*).

It should be emphasized that the poisoning molecules block the weak adsorption sites and not the strong ones despite the fact that the latter are favoured from the thermodynamic point of view. This explains why the intercept values of all the calibration curves in Fig. 2 are the same regardless of the treatment which has been applied to the palladium surface. The intercept value is directly proportional to the overall amount of the strong adsorption sites n_s (*11*) and it will remain constant in so far as the n_s value does not change. A possible reason for this behavior has been discussed elsewhere (*3*).

The effect of surface poisoning on the desorption of hydrogen from a thin palladium layer (α phase) is best illustrated in Fig. 7, where the desorption rate constants k_d, $k_d{}^I$ and the absorption second-order rate constant, k_a are plotted against the degree of poisoning, θ_{CS_2}. The three curves have the same shape and are of the "flexed linear" type (*8*), very similar to the well-known catalyst poisoning curves (*7*). The value of the sorption rates fall approximately linearly up to a certain stage of poisoning and after the inflection far less steeply with the increase of the degree of poisoning, without attaining the complete suppression of the process. A similar effect has been found by Maxted and Evans during the adsorption of hydrogen on Pt black catalyst poisoned with H_2S. The decrease of the adsorption rate of hydrogen was also of the flexed linear type and occurred in similar manner with the depression of the catalytic activity for the hydrogenation of crotonic acid (*9*). Taking into account the close similarity of these two metals in their catalytic properties it is justified to assume that the weakly bound hydrogen atoms on the palladium surface are involved in any catalytic reaction occurring at low partial pressure of hydrogen (α phase palladium–hydrogen catalyst), and that they are chiefly supplied by the dissolved atoms with which they are in a fast dynamic equilibrium.

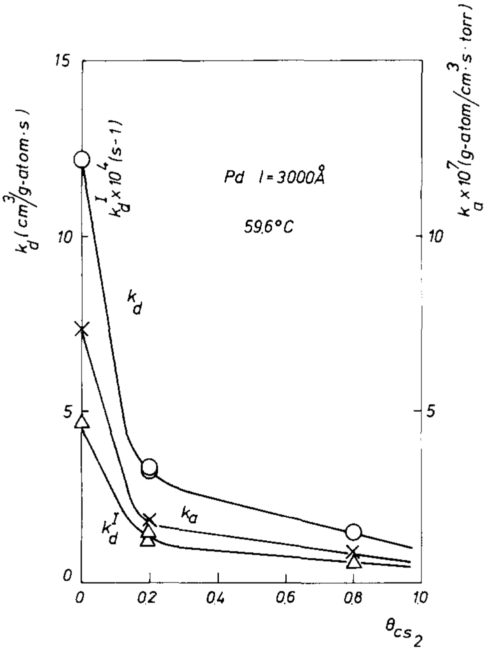

FIG. 7. Absorption and desorption rate constants in the α-region of the (Pd–H) system as a function of the degree of poisoning with CS_2.

CONCLUSIONS

Our major conclusions may be summarized as follows:

1. The desorption rate of hydrogen from α-palladium hydride decreases appreciably by poisoning its surface with CS_2 molecules, while the amount of hydrogen uptake (adsorbed and absorbed) is not at all affected.
2. Both stages by which hydrogen is removed from palladium are influenced by CS_2 poisoning, namely, the removal of the dissolved hydrogen by a transfer–recombination stage and the removal of the strongly bound hydrogen by a surface migration–recombination stage.
3. The effect of poisoning lies in the apparent diminution of the permeation sur-

face area, where the weakly bound hydrogen is located, without affecting their areal density. The poison seems to depress the surface mobility of the H_w atoms.

4. The change of the desorption and absorption rate constants obeys a flexed linear-type curve resembling catalyst poisoning curves. The α-palladium hydride catalyst is active through the weakly bound hydrogen chiefly supplied by the dissolved hydrogen with which it is in a fast dynamic equilibrium.

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