

## Hydrogen Spillover through Gas Phase Transport of Hydrogen Atoms

E. BAUMGARTEN, C. LENTES-WAGNER, AND R. WAGNER

*Institut für Physikalische Chemie I, der Universität Düsseldorf, Universitätsstr. 1, 4000 Düsseldorf, West Germany*

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Gas phase transport of hydrogen atoms was demonstrated using reducible substances (DPPH, anthracene, anthraquinone) on silica as a detector and Pd/SiO<sub>2</sub> as a source of atomic hydrogen. The reaction rates—followed by FTIR—clearly changed with the distance between source and detector sample. All changes in spectra were in full agreement with expectations for the hydrogenation of the test substances. © 1989 Academic Press, Inc.

### 1. INTRODUCTION

In a former investigation (1) we used FTIR to detect hydrogen atoms formed on a platinum metal (Pd) and spilled over to a silica surface carrying a reducible substance. Diphenylpicrylhydrazyl (DPPH), a stable radical, that may react with hydrogen atoms to the corresponding hydracine (DPPHN), was used as a detector substance. One most important problem is still unsolved: What is the mechanism by which hydrogen atoms migrate to the detector? In principle three ways have to be discussed: (a) gas phase transport, (b) surface diffusion, and (c) bulk diffusion.

Normally bulk diffusion is not taken into consideration, though it cannot be excluded from the experiments. Most authors try to explain their experiments with a surface diffusion model, i.e., Kramer and Andre (2) and Kramer (3) take surface diffusion as the rate determining step. Ambs and Mitchell (4) interpret the accelerating action of water as a kind of bridge from Pt to the oxide surface. Cavanagh and Yates (5) investigated H-D exchange on an alumina surface and discussed migrating hydrogen atoms at the surface. For systems of this kind we have shown that surface exchange processes may greatly contribute to the transport of the isotropic species (6), so this sys-

tem is not suited to solve the problem given here.

Few authors give indications for the existence of a gas phase transport. Lobashina *et al.* (7-9) discuss a surface diffusion without excluding a gas phase transport. The most convincing experiments were made by Ekstrom *et al.* (10, 11), reducing UO<sub>3</sub> via the gas phase at 673 K. Bianchi *et al.* (12) interpreted the reduction of methoxyl groups to methane at 703 K as a gas phase reaction of H<sub>3</sub>.

Considerable doubts about the possibility of a desorption of atomic hydrogen from a platinum metal may arise from thermodynamic arguments (Fig. 1). As dissociatively adsorbed hydrogen is in a lower energy state than H<sub>2</sub> gas, the desorption of H atoms should be less probable than the dissociation of hydrogen molecules.

Despite these discouraging facts we began our experiments because we repeatedly observed indications of gas phase reactions during HD exchange reactions; these observations were not published until now because we could not absolutely exclude the possibility of transport by the smallest traces of water vapor.

### 2. EXPERIMENTAL

A wafer of silica, carrying a reducible substance ("detector sample"), is posi-

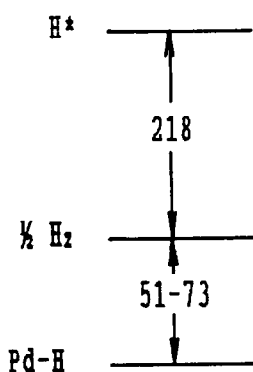


FIG. 1. Energy scheme for dissociation and adsorption of hydrogen on palladium.

tioned in the IR beam within a measuring cell (Fig. 2), similar to that described earlier (13). The position of a second sample, consisting of a ring of Pd/SiO<sub>2</sub> ("source sample"), could be changed. In the case of a gas phase reaction catalyzed by the source sample the reaction velocity should depend on the distance of the samples.

The samples were prepared from Aerosil (Degussa). The source sample was impregnated with PdCl<sub>3</sub> and reduced with H<sub>2</sub> at 473 K. This material was compressed into wafers (outer diameter, 22 mm; inner diameter, 16 mm).

The detector wafers were impregnated with solutions of the reducible substances. The following substances were used: DPPH (Aldrich >95%), anthracene (Aldrich, 99.9%), decadeuteroanthracene (Merck, 99% D), and anthraquinone (Aldrich, 97%, two times recrystallized from benzene). The position directly opposite to the detector sample (5 mm from the source) is called position 1, and the position about 100 mm away is called position 2. An aperture, just in front of the cell ( $\approx 3$  cm from the sample), was applied to avoid an illumination of the source ring.

Before admission of hydrogen the samples were pretreated at the reaction temperature for 1 h in helium. During the reaction time 9300 Pa of H<sub>2</sub> or D<sub>2</sub> was added to the stream of He (50 ml/min). The reaction temperature (333–373 K) was chosen to desorb as much water as possible without decomposition of the detector substance and to keep the sample in a stable adsorption-desorption equilibrium with respect to water during the experiments.

For reference measurements H or D atoms were used, produced in a high frequency discharge (Leybold HF generator, 45 kHz, about 10 Pa H<sub>2</sub> or D<sub>2</sub>).

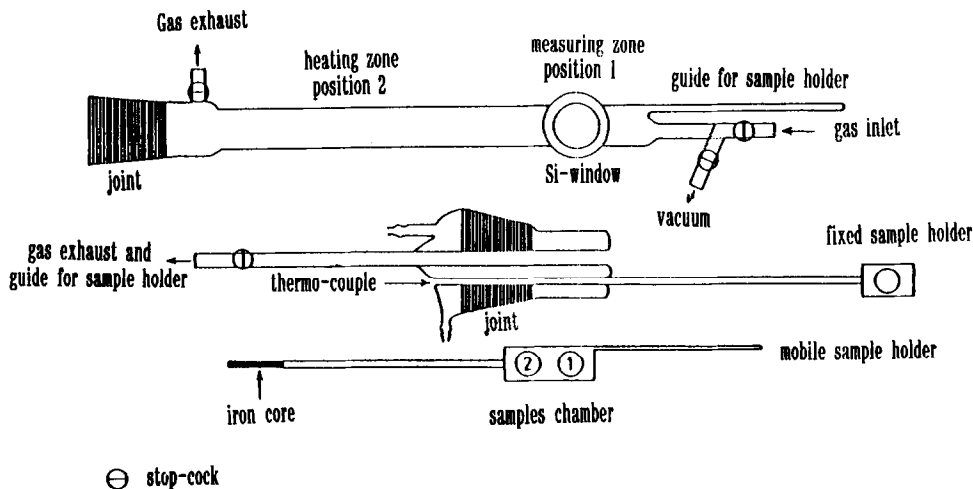


FIG. 2. Measuring cell.

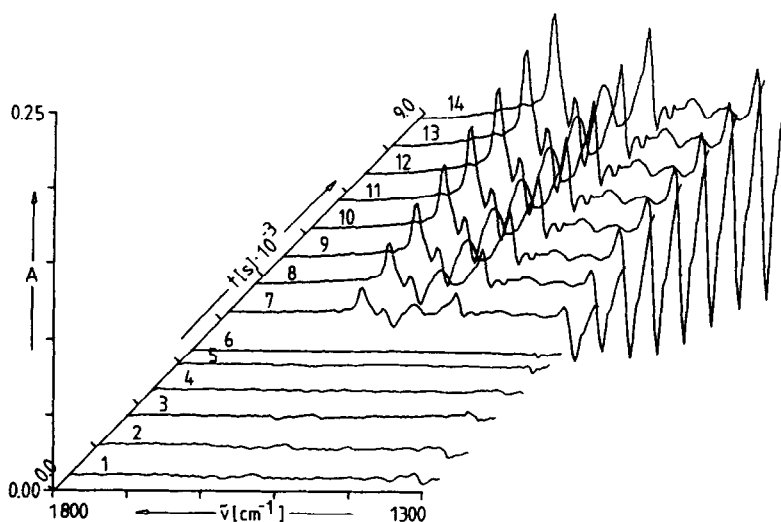


FIG. 3. Reaction of DPPH (1,1-diphenyl-2-picrylhydrazyl) with hydrogen atoms produced by high frequency discharge ( $T = 298$  K, duration of discharge 60 s each; reference, last spectrum before energization of the discharge). Spectra 1–2, sample in vacuum; spectra 3–6, sample in hydrogen, without discharge; spectra 7–14, sample in hydrogen, 1 min of discharge between each spectrum.

### 3. RESULTS AND DISCUSSION

#### 3.1. Experiments with DPPH

DPPH was chosen as the first detector material for possible gas phase hydrogen atoms, as it was found to be thermally stable enough for the investigations and to react with hydrogen atoms, forming a well-defined product (1). As mentioned under experimental, the possibility of a reaction of gas phase H atoms with the detector substance was tested by applying a high frequency discharge. With DPPH the change in the spectra obtained in this way (Fig. 3) was the same as that expected for the reaction in question (1).

In a greater number of experiments this system was tested for spillover by changing the position of the source sample.

Figures 4a and 4b show the time dependence of the spectra for the N–H valence band and the deformation region (during spectra 1–5 no hydrogen was in the cell); spectra 6 and 7 were obtained with the source sample in position 2, in great distance, spectra 8 to 12 with the source oppo-

site to the detector sample (position 1), and finally spectra 13 and 14 with great distance again. The spectra obtained in this way agree very well with those obtained during the high frequency discharge. Even the N–H valence band could be observed though it has a small extinction coefficient and is situated in a spectral region, where the signal-to-noise ratio is not optimal. Figures 5a–5d show a complete evaluation of the integral absorbances of the spectra obtained during this experiment, showing more clearly the changes in reaction velocity with position of the source sample.

The principal possibility of a transport of DPPH to the Pd particles and of the hydrogenation product back to the detector wafer may be ruled out with the following arguments:

(i) The volatility of DPPH is very low; it is not known whether this substance sublimes without decomposition.

(ii) During the initial part of the experiments, while only helium is passing over the sample, no loss of DPPH was to be seen.

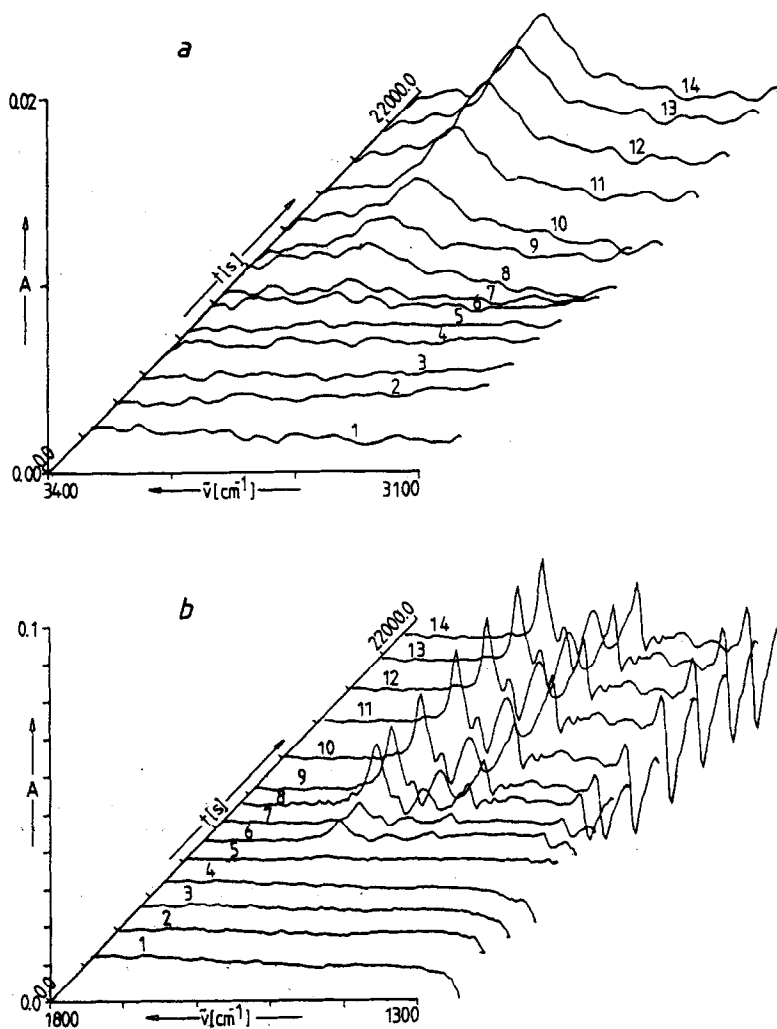


FIG. 4. Gas phase hydrogen spillover from Pd/SiO<sub>2</sub> detected with DPPH (selected spectra) ( $T = 333$  K; reference, last spectrum before admission of H<sub>2</sub>, at  $t = 8318$  s). (a) N-H valence band; (b) deformation region (as in Fig. 3).

(iii) On Pd crystallites the hydrogenation should not stop at the "intermediate" observed here, and the aromatic rings should be hydrogenated too. This effect was observed indeed on a wafer with Pd on an outer ring only and DPPH on the whole sample. In the direct vicinity of the Pd particles the hydrogenation led to an uncolored product, while both the DPPH and the primary reaction product (the hydrazine) are violet or orange red, respectively.

### 3.2. Experiments with Anthracene and Decadeuteroanthracene

In an earlier paper (14) we described experiments designed to find hydrogenation of benzoate species, adsorbed on alumina, which were not successful. The absence of hydrogenated species either may be explained the instability of the radical, formed as an intermediate from benzoate, or may indicate that Al<sub>2</sub>O<sub>3</sub> is a substance, catalyz-

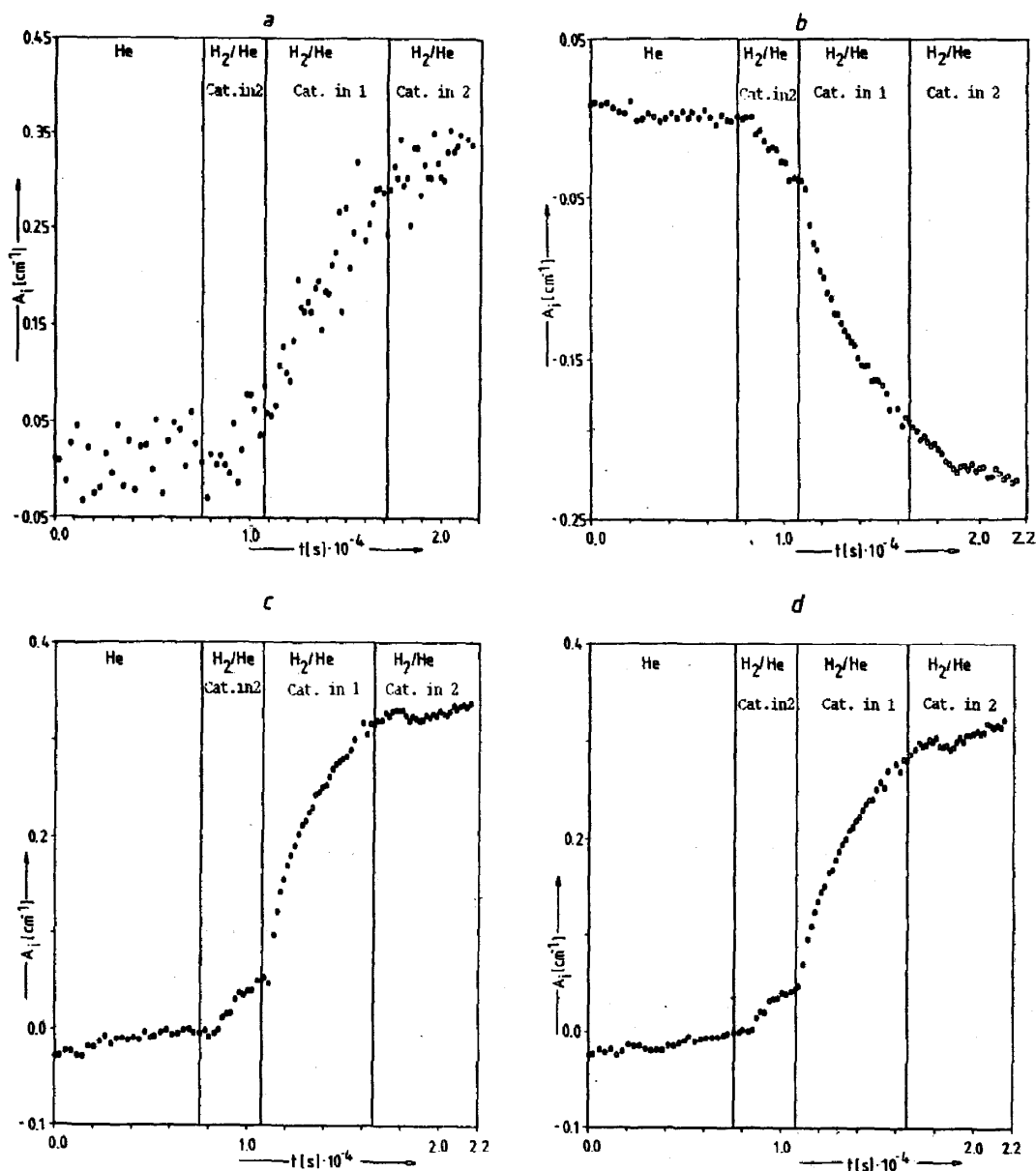


FIG. 5. Kinetics of conversion of DPPH by gas phase hydrogen spillover (complete measurement of Fig. 4). (a) N-H valence band integration limits, 3348.4–3248.1  $\text{cm}^{-1}$ ; (b) DPPH band integration limits, 1589.3–1550.8  $\text{cm}^{-1}$ ; (c) DPPHN band integration limits, 1577.8–1527.6  $\text{cm}^{-1}$ ; (d) DPPHN band integration limits, 1523.8–1481.3  $\text{cm}^{-1}$ .

ing the recombination of hydrogen atoms. So here we chose a system with detector substances which may form more stable intermediates: anthracene and perdeuteroanthracene, both of which were found to react

with H or D atoms, produced in a discharge.

Figure 6 again shows the influence of the position of the source sample on the reaction. In contrast to anthracene (the educt),

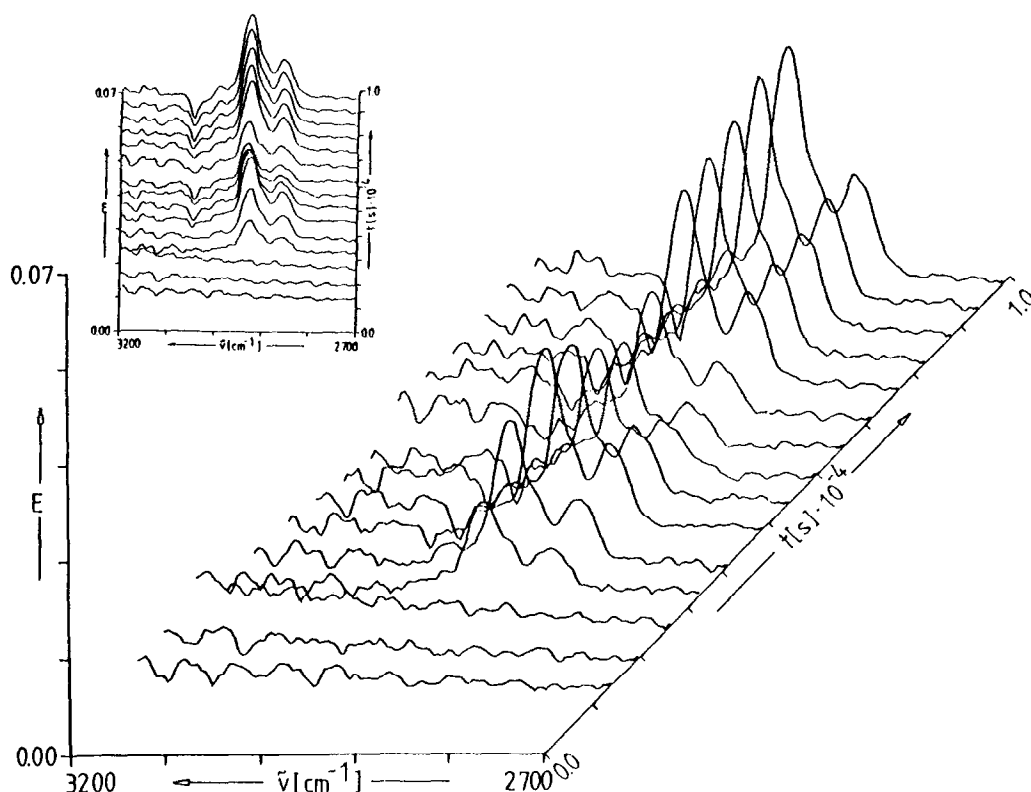


FIG. 6. Gas phase hydrogen spillover from Pd/SiO<sub>2</sub>. Detected with anthracene (selected spectra) ( $T = 353$  K; reference, last spectrum before admission of H<sub>2</sub>, at  $t = 2556$  s). Spectra 1–2: gas, He, position 1; spectra 3–6: gas, H<sub>2</sub>/He, position 1; spectra 7–9: gas, H<sub>2</sub>/He, position 2; spectra 10–15: gas, H<sub>2</sub>/He, position 1.

the product (9,10-dihydroanthracene) is slightly volatile at the reaction temperature (353 K); thus, the bands of the CH<sub>2</sub> groups grow, as long as the source sample is in position 1, as more product is formed than lost by vaporization. With the source sample in position 2, it decreases because vaporization is the faster reaction. This effect is seen even more clearly in Fig. 7, showing the integral absorbances for the anthracene/H<sub>2</sub> or those of anthracene-*d*<sub>12</sub>/D<sub>2</sub> (Fig. 8). H–D exchange of the hydroxyl bands of silica during the same experiment is shown in Fig. 9. The reaction is much faster than the hydrogenation of anthracene-*d*<sub>12</sub>. As the reaction was already complete after 1500 s, an effect of the distance of the source could not be observed under these conditions.

This effect was not investigated more thoroughly here, since H–D exchange may be caused by water vapor under the given conditions.

### 3.3. Experiments with Anthraquinone

Anthraquinone was employed in an additional test, because it is known to react with nascent hydrogen to form anthrone (15). The hydrogenation test with discharge-produced hydrogen was positive as with the other substances used. The progress of the spillover reaction is shown in Fig. 10 using the CH valence bands of anthrone. The results obtained with this system clearly show that hydrogen may be spilled over via the gas phase.

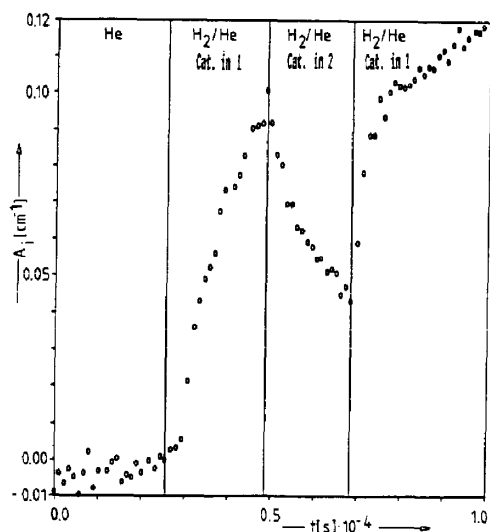


FIG. 7. Kinetics of conversion of anthracene by gas phase hydrogen spillover (complete measurement of Fig. 6). Formation (and vaporization) of 9,10-dihydroanthracene, as seen from aliphatic C-H valence band integration limits, 2974.2-2831.5  $\text{cm}^{-1}$ .

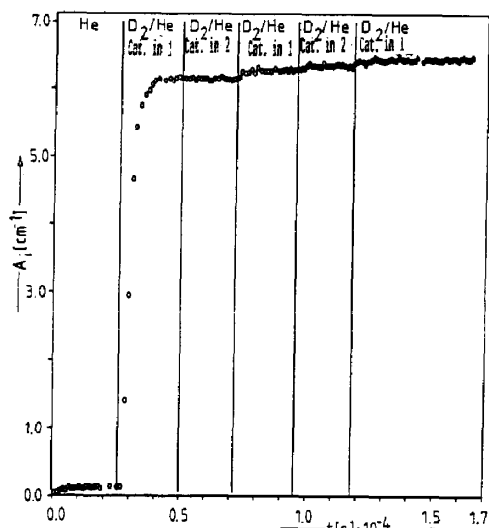


FIG. 9. H-D exchange of surface hydroxyl groups of  $\text{SiO}_2$  during the experiment of Fig. 8.

### 3.4. Discussion

A surface diffusion over the glass surfaces could be ruled out, as the distance

was more than 200 mm, and it was longer for position 1 than for position 2.

As mentioned in the Introduction, the thermodynamic arguments seemed to exclude the possibility of a gas phase hydro-

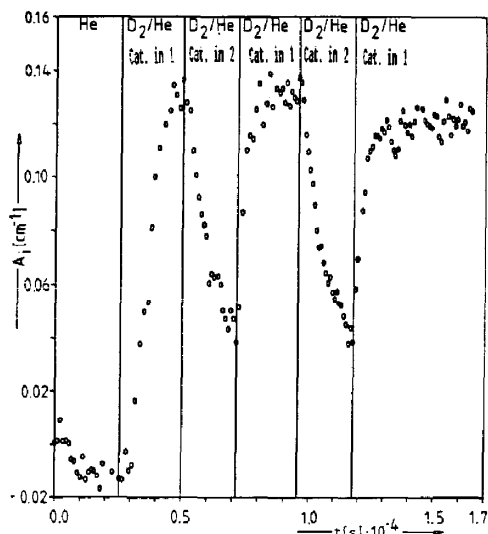


FIG. 8. Kinetics of conversion of anthracene- $d_{10}$  by gas phase deuterium spillover (353 K). Formation (and vaporization) of 9,10-dideuteroanthracene- $d_{12}$ : C-D valence band integration limits, 2225.9-2156.4  $\text{cm}^{-1}$ ; baseline, 2225.9-2060.0  $\text{cm}^{-1}$ .

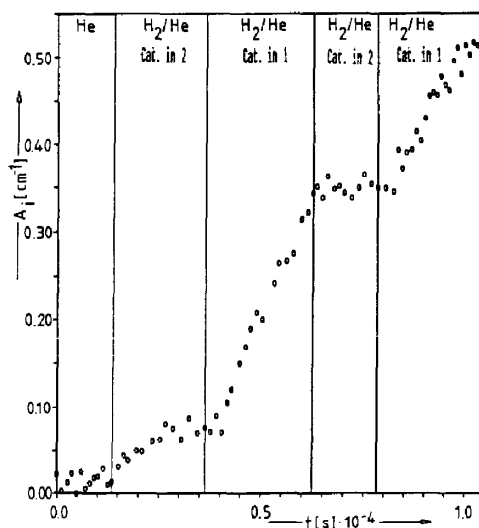


FIG. 10. Kinetics of conversion of anthraquinone by gas phase hydrogen spillover, forming anthrone ( $T = 373 \text{ K}$ ; reference, last spectrum before admission of  $\text{H}_2$ ). C-H valence band integration limits, 3016.7-2796.8  $\text{cm}^{-1}$ .

TABLE 1  
Adsorption Enthalpies of H<sub>2</sub> on Palladium

Surface	Heat of adsorption (kJ/mole)			Ref.
Pd-wire	92.1	104.7	146.5	(20)
Pd (111)	87.9	99.2		(21)
Pd (110)	102.2	96.3		(19)
Pd (100)	192.6	96.3		(22)

gen spillover; this was the cause for the extreme caution with which the described experiments were executed and for a great number of reproduction measurements for each experiment. We conclude that hydrogen atoms are desorbed from platinum metals even at low temperatures (350–400 K). From our measurements we cannot exclude a possible association of these hydrogen atoms, forming H<sub>3</sub> or H<sub>3</sub>O. Theoretical calculations seem to rule out this possibility (16, 17); mass spectroscopic measurements (18) reveal that both H· and H<sub>3</sub>O· are (meta)stable for about 1 μs.

It was not possible to explain the thermodynamics of the process completely. At least a part of the energy necessary for the formation of the hydrogen atoms may be gained by the following process: Under the given experimental conditions noble metals are covered nearly completely with hydrogen in atomic form. If a further hydrogen molecule is adsorbed on a single site completely surrounded by adsorbed hydrogen already, then only one atom of the molecule may be adsorbed, but the adsorption energy of this atom may only partially compensate the dissociation energy of the hydrogen molecule. From Fig. 1 it follows that the average adsorption energy is not sufficient to break the hydrogen–hydrogen bond. Table 1 gives adsorption enthalpies for hydrogen on palladium. In the case that hydrogen atoms may be stabilized by H<sub>2</sub> or H<sub>2</sub>O in the gas phase, this effect might facilitate the formation of the active species.

An additional experiment was per-

formed, using a platinum wire, lying on the bottom of the measuring cell. Even in this experiment hydrogen was spilled over via the gas phase; thus the effect is neither restricted to palladium as a metal nor is a high dispersion of the metal, and the presence of a carrier absolutely necessary.

From these experiments one cannot exclude a parallel surface diffusion of hydrogen atoms in spillover processes. On the other hand the reaction rates observed here may be great enough to explain the velocity of H–D exchange on the oxide sample containing some noble metal (6, 19) if one takes into regard that under these experimental conditions the hydrogen atoms have only to migrate over very short distances, before they may react with a surface hydroxyl group. After this initial step the further transport may be due to exchange diffusion described earlier (19). On the other hand—in our case—most hydrogen atoms will be lost by recombination on their way out of the source sample and through the gas phase, where recombination and loss with the streaming gas may occur. Moreover the reaction of hydrogen atoms with the detector substance may be sterically hindered and restricted to the outer layer of the hydrogenatable organic substance. Because of these limitations no attempt was made here to estimate the flux of hydrogen atoms, being produced on the Pt surface.

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