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Hydrogen Spillover through Gas Phase Transport of Hydrogen Atoms

Reply to M. S. Spencer, R. Burch, and S. E. Golunski

Spencer, Burch, and Golunski (*1*) discuss our results on hydrogen spillover through the gas phase (*2*), results which are more completely described in (*3*). As in (*4*), the gases were all purified by being passed through Oxysorb (Messer Griesheim), thus reducing the oxygen content to 0.02 ppm (*5*). The final reaction mixtures were passed over a Pt/Al_2O_3 catalyst at 473 K and through a cold trap (molecular sieve 3 Å, 77 K), so that the last traces of oxygen could react to water in case of H_2/He or D_2/He, and the water could be adsorbed by the cold traps. The efficiency of the gas purification is demonstrated by the fact that a wafer of Pt/alumina, preheated to 1070 K, showed no increase in OH absorbance during the passage of reaction gas (H_2/He). Figure 1 shows the experimental setup.

On the basis of the experimental conditions, it follows that we did not discuss oxygen as a possible reactant for an "energizing reaction" as proposed by Spencer *et al.* (*1*).

Because of its small concentration, oxygen was also not considered to be a "complexing" agent. H_2 and H_2O were mentioned in this respect—although $H_3^{\cdot}$ and $H_3O^{\cdot}$ are not very stable—to show that $H^{\cdot}$ is not necessarily the *only* radical species in the gas phase.

We have made estimations of the minimum H-atom flow rate necessary for the conversion of the test substances. Integral extinction coefficients (A') were determined from difference spectra of reactant and reaction product (equal concentrations, 1% each in KBr). For DPPH and the reaction product (diphenyl-picryl-hydrazine) and the spectral interval 1589–1550 cm^{-1}, for example, A' is 5.7×10^6 cm mol^{-1}. From the initial change in absorbance in the respective interval ($dA/dt = 5.3 \times 10^{-5}$ $cm^{-1}\ s^{-1}$), one obtains a flow rate j of $H^{\cdot}$ (at the detector surface) given by

$$j = \frac{dA_i}{dt} \cdot \frac{1}{A'}\,\nu,$$

where ν = stoichiometric factor. In this example, $\nu = 1$ (1 $H^{\cdot}$/DPPH) and $j = 9.3 \times 10^{-12}$ mol/cm^2 s. Average values are given in Table 1.

Model calculations were executed to determine the flow rate of H-atoms at the surface of the source wafer (differing by the amount of recombination).

The gas phase between the wafers was divided into 20 compartments. Transport by diffusion and recombination were calculated using the values D_H in $H_2 = 2.92\ cm^2\ s^{-1}$ (T = 372 K) (*6*) and $k_{rec} = 2 \times 10^{16}\ cm^6\ mol^{-2} \cdot s^{-1}$ (*7*). The results are compiled in Table 1 together with the oxygen flows necessary for complete consumption of reac-

TABLE 1

Flow Rates of $H^{\cdot}$ during Gas Phase Hydrogen Spillover as Obtained from Initial Reaction Rates

T (K)	Substance	$j_{H^{\cdot}}$ (mol/cm^2 s)	$j_{O\,H^{\cdot}}$ (mol/cm^2 s)	$j_{0\,O_2}$ (mol/cm^2 s)	c_{O_2} (ppm)
333	DPPH	1.0×10^{-11}	1.1×10^{-11}	5.5×10^{-12}	0.15
353	Anthracene	2.1×10^{-10}	6.0×10^{-10}	3.0×10^{-10}	8.1
373	Anthraquinone	1.2×10^{-10}	1.7×10^{-10}	8.5×10^{-11}	2.3
348	H/D exchange	3.7×10^{-10}	1.3×10^{-9}	6.5×10^{-10}	17.5

Note. $j_{H\cdot}$, flow rate of $H\cdot$ at surface of detector wafer. $j_{O\,H\cdot}$, flow rate of $H\cdot$ at surface of source wafer. $j_{0\,O_2}$, minimal flow rate of O_2, which could produce the combustion energy necessary to give $j_{O\,H\cdot}$. c_{O_2}, minimal oxygen concentration in gas stream, necessary to give $j_{O\,H\cdot}$.

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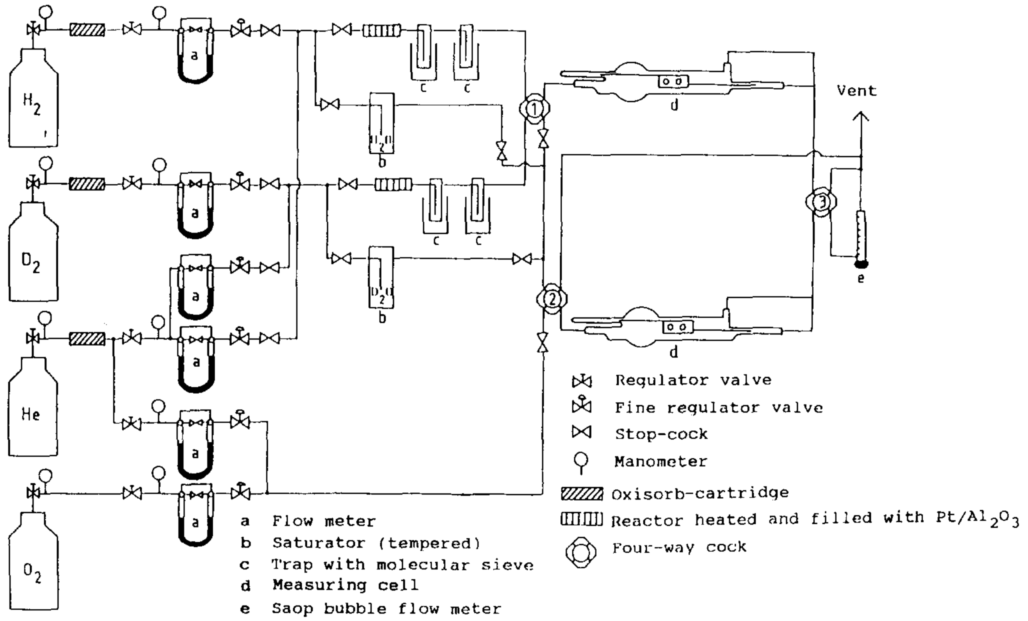

FIG. 1. Experimental setup for purification and mixing of gas streams.

tion energy of the reaction

$$O_2 + 2\,H \rightarrow 2\,H_2O$$

to desorb $H^\cdot$ from Pd ($\Delta H_{f(H_2O)}$) = −285.9 kJ/mol (*5*); ΔH_{desorb} = 269 − 291 kJ/mol (*2*)). With a gas flow of 50 ml/min, minimal oxygen contents are obtained. These values clearly exceed the oxygen content of the gas stream.

We also considered other sources of energy (including even cold fusion which was being intensively discussed at the time of the investigations), but we did not mention this, as no positive results were obtained.

Finally it should be mentioned that any "energizing" reaction considered in a gas phase transport during spillover would also apply to normal spillover experiments, provided that the reaction gas was not purified further and other side reactions could be excluded.

We therefore think that desorption of hydrogen atoms into the gas phase, whatever the explanation of the source of energy, is at least one reaction path in hydrogen spillover.

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