

LETTERS TO THE EDITOR

Comments on "Hydrogen Spillover through Gas Phase Transport of Hydrogen Atoms"

In a recent paper Baumgarten *et al.* (1) found evidence for hydrogen spillover through the gas-phase transport of hydrogen atoms from a palladium/silica catalyst to several reducible adsorbed molecules (diphenylpicrylhydrazyl (DPPH), anthracene, anthraquinone) supported on silica. They showed unequivocally that, although catalyst and organic reactant molecules were separated physically, both catalyst and gaseous hydrogen were required for hydrogenation of the molecules. These results are surprising, especially in view of the low reaction temperatures used (333–373 K), as indeed the authors recognised. An earlier analysis by Levy and Boudart (2) indicated that temperatures greater than 800 K would be required for free hydrogen atom formation to be significant in typical catalytic systems. It is not surprising that Baumgarten *et al.* (1) found some difficulty in the interpretation of their results: for instance, they write "It was not possible to explain the thermodynamics of the process completely" (1).

We believe that a valid analysis of the system can be made by use of the appropriate equilibrium concentration of hydrogen atoms in the gas phase, $[H\cdot_{(g)}]_{\text{equ}}$. Then the following model is a qualitatively plausible interpretation of the system of Baumgarten *et al.*:

1. DPPH is hydrogenated by the reaction of gas-phase hydrogen atoms, either directly or via prior adsorption on the silica wafer.

2. In the absence of the palladium catalyst the gas-phase concentration of hydrogen atoms, $[H\cdot_{(g)}]$, is much less than the equilibrium value because of the slow ho-

mogeneous dissociation of H_2 molecules and fast removal of $H\cdot_{(g)}$ atoms on the various surfaces present (DPPH, silica, glass, etc). The hydrogen feed, presumably at ambient temperature, into the apparatus cannot contain the equilibrium concentration of hydrogen atoms corresponding to the reaction temperature.

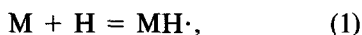
3. In the presence of the palladium catalyst, equilibration between gas-phase H_2 and adsorbed hydrogen species is fast, so this achieves gas-phase equilibration, i.e., $[H\cdot_{(g)}] \sim [H\cdot_{(g)}]_{\text{equ}}$. Thus the catalyst provides a supply of gas-phase hydrogen atoms for DPPH hydrogenation.

4. There is no route by which $[H\cdot_{(g)}]$ can rise above $[H\cdot_{(g)}]_{\text{equ}}$ because no energy is fed into the system.

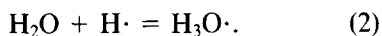
This simple model can be tested for the most favourable conditions: $[H\cdot_{(g)}] = [H\cdot_{(g)}]_{\text{equ}}$ is maintained by the separate Pd/silica wafer and the maximum rate of hydrogenation of DPPH (diphenylpicrylhydrazyl) is given by the collision rate of $H\cdot_{(g)}$ with the total surface of the silica wafer carrying the DPPH. With data from Fig. 5a of Ref. (1), reaction time was 6400 s, $[H_2] = 9330$ Pa and the temperature (not given directly) is taken to have been 350 K. The surface area of the silica wafer is calculated to be 3.3 m^2 from data in an earlier publication (3). Then the value of $[H\cdot_{(g)}]_{\text{equ}}$ is 3.4×10^{-26} Pa and the maximum amount of product formed can have been about 100 molecules only (cf. about 6×10^{17} molecules of DPPH on the wafer). Thus gas-phase transport of hydrogen atoms cannot account for the observation of Baumgarten *et al.* (1) by many orders of magnitude.

One way of increasing the effective con-

centration and flux of gas-phase H atoms could be via complex formation, e.g.,



where the conditions and K_1 are such that $[MH \cdot_{(g)}]/[H \cdot_{(g)}] \gg 1$. Baumgarten *et al.* (1) suggested two candidates for M, H_2 , or H_2O , so that $MH \cdot_{(g)}$ is either $H_3 \cdot_{(g)}$ or $H_3O \cdot_{(g)}$. The first, $H_3 \cdot_{(g)}$, can be rejected because there is no hollow in the H– H_2 reaction plot. The $H_3 \cdot_{(g)}$ observed by mass spectrometry (4) must be an electronically excited state and so it is irrelevant for gas-phase transport considered here. A $H_3O \cdot_{(g)}$ species has been claimed (4) to have a lifetime of $>1 \mu s$, then the activation energy is about 40 kJ mol^{-1} , and the maximum value of $\Delta H^\circ_{(2)}$ is about -40 kJ mol^{-1}



To the accuracy needed here, we can take the preexponential term of K_2 to be the same as that for reaction (3), about 10^{-12} Pa^{-1} ,



Then the maximum values of K_2 are given by

$$K_2 = 10^{-12} \exp(40,000/8.3T) \text{ Pa}^{-1} \quad (4)$$

and at 350 K, $K_2 \approx 10^{-6} \text{ Pa}^{-1}$. The partial pressure of water was not measured in the system of Baumgarten *et al.* but we can take 100 Pa as a plausible upper limit. Then $H_3O \cdot$ concentration is given by

$$\frac{[H_3O \cdot_{(g)}]}{[H \cdot_{(g)}]} = K_2[H_2O] < 10^{-4}. \quad (5)$$

Thus the concentration of $H_3O \cdot_{(g)}$ is much lower than $[H \cdot_{(g)}]$ and it would need to be at least 10^{10} larger to account for the experimental results. It is improbable that any acceptable parameter adjustment could give this increase: indeed if $H_3O \cdot_{(g)}$ were sufficiently stable to contribute to hydrogen transport, its existence would have been recognised more widely than the fleeting passage in a mass spectrometer. Approximate

calculations indicate that $\Delta H^\circ_{(2)}$ would have to be $\sim -125 \text{ kJ mol}^{-1}$. It is clear then that complex formation cannot provide an explanation for the observed results.

As both hydrogen and the Pd/SiO₂ wafer are needed for hydrogenation of DPPH, the catalyst must raise $[H \cdot_{(g)}]$ to levels many orders of magnitude higher than $[H \cdot_{(g)}]_{\text{equ}}$. This could be achieved only by the input of energy to the catalyst and two sources of energy can be suggested: the IR beam used for spectroscopy and parasitic exothermic reactions. As Baumgarten *et al.* (1, 3) concentrated the IR beam *within* the Pd ring on the wafer, it is unlikely that the Pd crystallites were heated to a temperature high enough to give the necessary increase in $[H \cdot_{(g)}]$. Parasitic exothermic reactions provide a more plausible explanation. Baumgarten *et al.* (1) do not give gas purities but in an earlier paper by the same group (5) helium purity was quoted as 99.996% (it is not clear whether helium was further purified, as was their hydrogen). Let us suppose that the helium stream contained an oxygen impurity of 1 ppm (cf. total quoted impurity of 40 ppm). Then the enthalpy change produced by the combustion of hydrogen from this oxygen, during the total time of helium flow (17,200 s), was 0.28 J. This energy, if used solely in the dissociation of H_2 , would have given 8×10^{17} H atoms, which is more than sufficient to hydrogenate all the DPPH molecules present ($\sim 6 \times 10^{17}$ molecules).

Thus the reaction of very low levels of oxygen impurity could overcome the thermodynamic limit on gas-phase transport. The energy efficiency of $H \cdot_{(g)}$ formation in any parasitic process must depend on the mechanism of the process. Several mechanisms, all involving the palladium catalyst, appear plausible. The desorption of OH, formed by O₂/H₂ reaction on Pd, followed by the gas-phase reaction $OH + H_2 \rightarrow H_2O + H$ would provide $H \cdot_{(g)}$. The desorption activation energy of OH from Pt surfaces is (6) only about 120 kJ mol^{-1} . Similarly the formation and desorption of HO₂· by the reaction of H_(a) and O₂ on the Pd surface,

followed by reactions with H_2 is another possibility. It needs to be emphasized that because the equilibrium partial pressure of $H\cdot$ at 350 K in this system is so low (3.4×10^{-26} Pa, i.e., only about 7×10^{-9} molecule dm^{-3}), even slow and inefficient parasitic reactions of traces of oxygen could raise the actual value of $[H\cdot(g)]$ to far above this equilibrium value.

In principle, traces of oxygen could also promote gas-phase transport of hydrogen atoms by complex formation. The radical $HO_2\cdot$ is sufficiently stable ($\Delta H_f^\circ \sim +10$ kJ mol^{-1} , so $\Delta H^\circ \sim -206$ kJ mol^{-1} for the reaction $H\cdot + O_2 = HO_2\cdot$) for it to be a H-carrier through the gas phase. However, its rate of formation in the gas phase under the experimental conditions of Baumgarten *et al.* is too slow by many orders of magnitude. The rate constant of reaction (6) is given (7) as 2.5×10^{-32} (cm^3 molecule $^{-1}$) 2 s^{-1} (for $M = He$) and for $[O_2] = 40$ ppm, the maximum value on quoted purity, and $[H\cdot(g)] = [H\cdot(g)]_{equ}$, the rate of formation of $HO_2\cdot$



is only about 400 molecule cm^{-3} s^{-1} .

There is evidence from at least two other contrasted systems that gas-phase transport of hydrogen atoms is not a general phenomenon at low to moderate temperatures. Levy and Boudart (2) observed rapid spillover in an intimate physical mixture of Pt/SiO₂ and WO₃ at about 300 K, but with the components separated under gaseous hydrogen "no reduction took place even after 2 yr." Zhang *et al.* (8) found that Pd enhanced the reduction of Co²⁺ in NaY zeolite but only when Pd²⁺ and Co²⁺ were in the same zeolite cage. There was no hydrogen spillover across greater distances, either through the gas phase or across the zeolite internal surface.

We have shown elsewhere (9) that gas-phase transport of hydrogen atoms makes a negligible contribution to the hydrogen spillover observed in methanol synthesis with Cu/ZnO/Al₂O₃ catalysts and with physical mixtures of Cu/SiO₂ and ZnO/

SiO₂ catalysts. Further, in these practical catalytic systems, parasitic reactions of, for example, traces of oxygen are not significant. In this context it is worth emphasizing Dowden's observation (10) that phenomena attributed to spillover in some very slowly reacting systems (similar to DPPH hydrogenation) may not be relevant to practical catalysis.

In summary, our view is that the hydrogenation of DPPH and other molecules observed by Baumgarten *et al.* (1) below 400 K cannot be explained in terms of hydrogen spillover by the gas-phase transport of hydrogen atoms. The reactions of very small traces of oxygen, present in the helium carrier gas, on the palladium catalyst could provide an alternative source of hydrogen atoms.

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