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ON THE H_2–D_2 EXCHANGE ON STEPPED PLATINUM SURFACES

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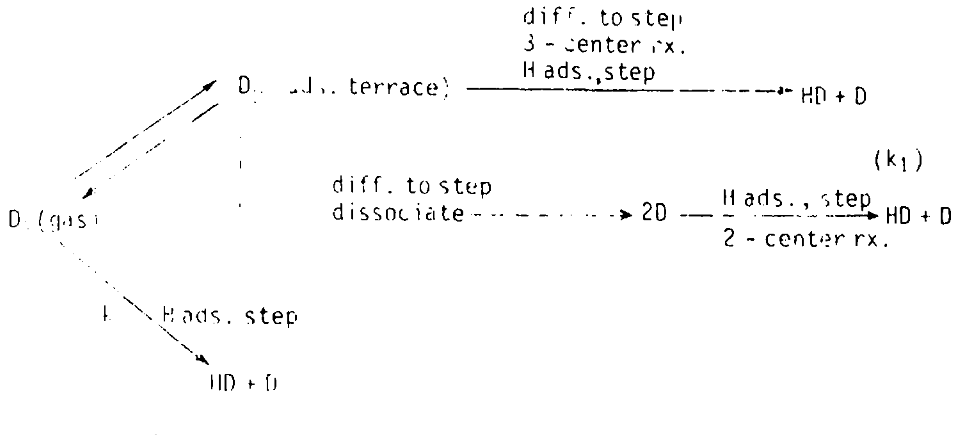
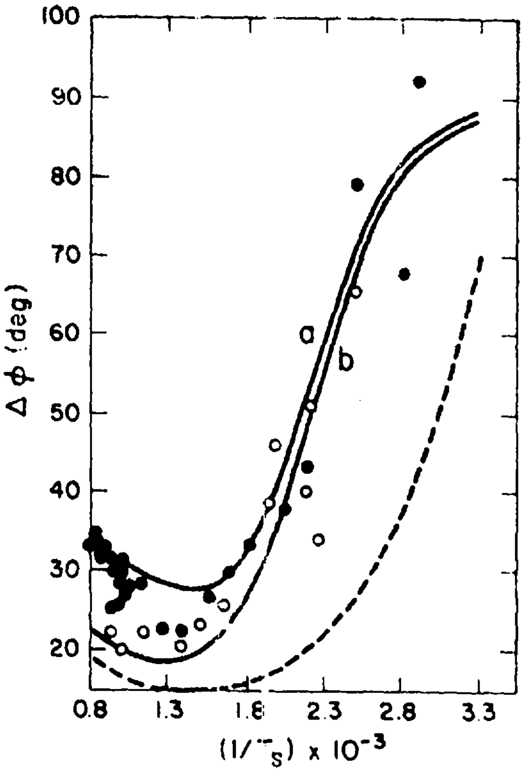
The hydrogen–deuterium exchange on stepped (111) platinum surfaces was recently investigated by Bernasek and Somorjai using modulated beam relaxation spectrometry (MBRS) [1]. These authors reported that stepped surfaces were 10^3–10^4 times more efficient in the exchange reaction as the (111) face without measureable step concentrations. Lu and Rye, on the other hand, reported that probabilities of hydrogen adsorption on several crystal planes of Pt, including one with a high density of steps, varied by only twenty between the most active and least active surfaces [2]. In this work we present a reinterpretation of the rather complex data of Bernasek and Somorjai on the basis of a simple branched-step mechanism which (1) represents the data of Bernasek and Somorjai more accurately than the original mechanism proposed, (2) indicates that an alternate reaction channel was accessible on the surfaces cut to produce steps, and (3) indicates that the increase in exchange probability on the stepped surfaces was approximately twenty, in agreement with the results of Lu and Rye.

The original data of Bernasek and Somorjai are presented in figs. 1–4. Their calculated values for the observed behavior, shown as dashed lines on these figures, resulted from the following branched mechanism



For this process the rate constants k_1 and k_2 were calculated to be

$$2 \times 10^5 \exp\left(-\frac{4.5\ \text{kcal/gmole}}{RT}\right) \text{sec}^{-1} \quad \text{and} \quad 10^2 \exp\left(-\frac{0.6\ \text{kcal/gmole}}{RT}\right) \text{sec}^{-1}$$



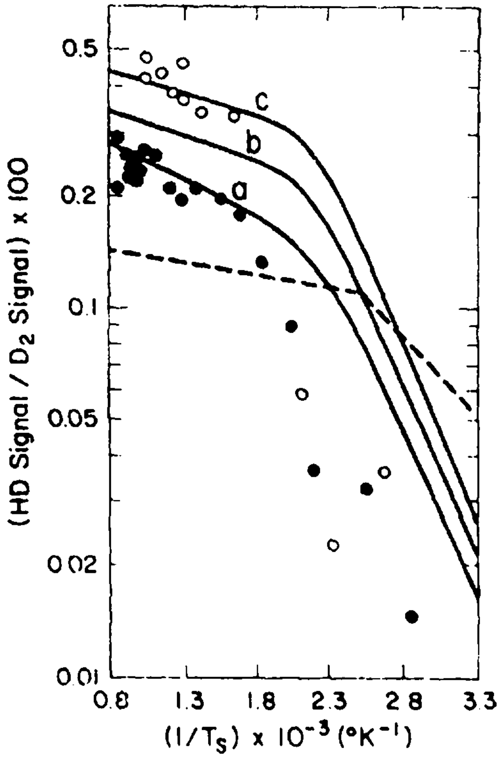


Fig. 1. HD phase-lag versus reciprocal surface temperature at 40 Hz: (●) Pt-S[9(111) × (111)]; (○) Pt-S[5(111) × (111)], dashed line, Bernasek and Somorjai; solid lines, this work curve (a) Pt-S[9(111) × (111)], curve (b) for Pt-S[5(111) × (111)].

Fig. 2. Relative HD amplitudes at 40 Hz, (●) Pt-S[9(111) × (111)]; (○) PtS[5(111) × (111)]; dashed line, Bernasek and Somorjai, solid lines, this work; curve (a) Pt-S[9(111) × (111)], curve (b) Pt-S[5(111) × (111)], curve (c) is curve (b) times 1.30.

for the pseudo-first-order rate constants, respectively. The branching probability P was taken to be 0.5 for both the Pt-S[9(111) × (111)] and the Pt-S[5(111) × (111)] surfaces [also designated as Pt(997) and Pt(553), respectively]. The authors proposed the second reaction process represented by k_2, to account for the phase reversal and the change in the slope of the amplitude at high temperatures. This mechanism necessitated direct collision of incoming reactants with hydrogen atoms adsorbed at steps on the surface; though possible, such a collisional encounter seems highly unlikely, particularly since the total reaction probability was estimated to be 0.1 [1], and since the surface coverage by hydrogen atoms above 800 K must be quite low.

In agreement with Bernasek and Somorjai, we have utilized a branched process on a surface of heterogeneous reactivity to explain the data. However, our calculations were made assuming a simple branched mechanism with two parallel steps for HD formation which occur subsequent to adsorption. In the model we assumed that, subsequent to adsorption, the slowest reaction step for HD production in each branch was the result of interaction with two different sites on the Pt surface

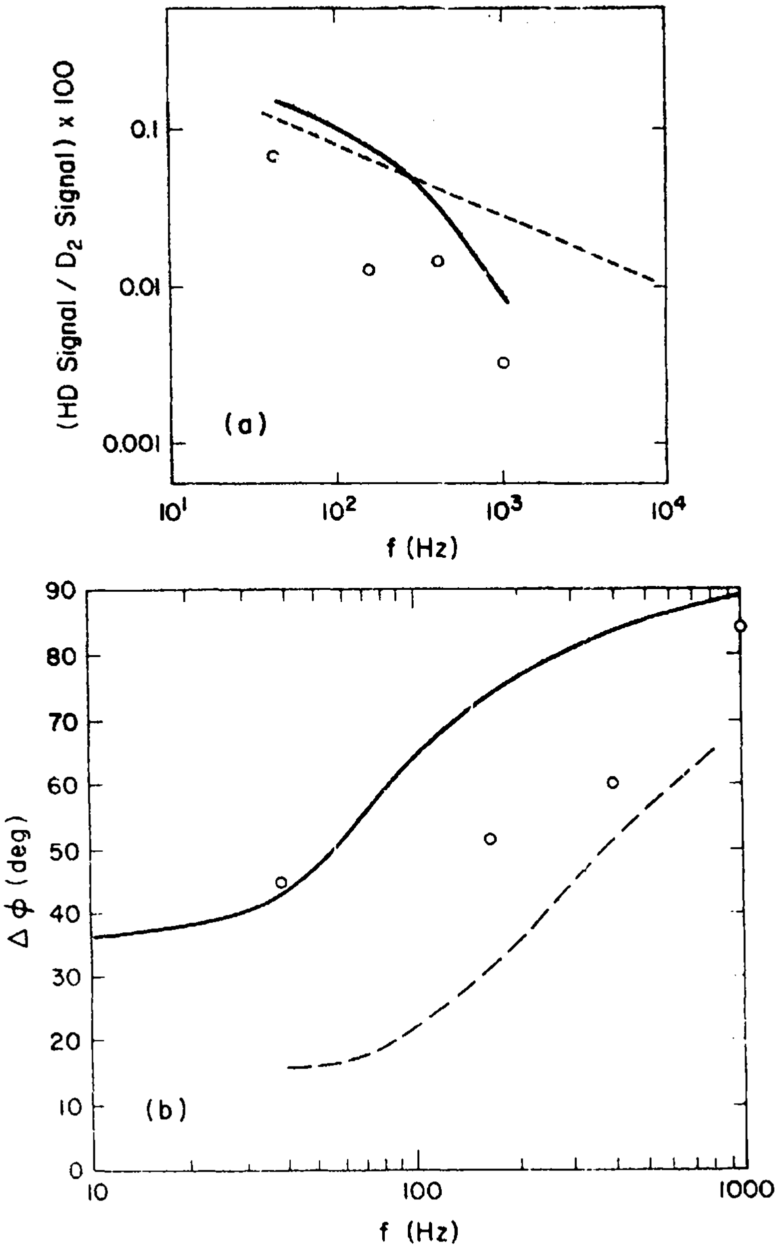


Fig. 3. (a) Relative HD amplitudes and (b) HD phase-lag at 485 K versus modulation frequency on Pt-S[9(111) × (111)]; (○) data of Bernasek and Somorjai; dashed line, analysis of B–S; solid line, this work. (The data points in this figure were plotted taking the data at 40 Hz of figs. 1 and 2 as locator points.)

those associated with the presence of steps (k_s) and those on the terrace (k_t). The respective branching probabilities were P_s and $P_t = (1 - P_s)$. The results of our analysis are shown as solid lines on figs. 1–4. The rate constant employed in the calculation were

$$k_s = 8 \times 10^4 \exp\left(\frac{-5.2\ \text{kcal/mole}}{RT}\right)\text{sec}^{-1}\ ,\quad k_t = 3 \times 10^2 \exp\left(\frac{-2.7\ \text{kcal/gmole}}{RT}\right)\text{sec}^{-1}\ ,$$

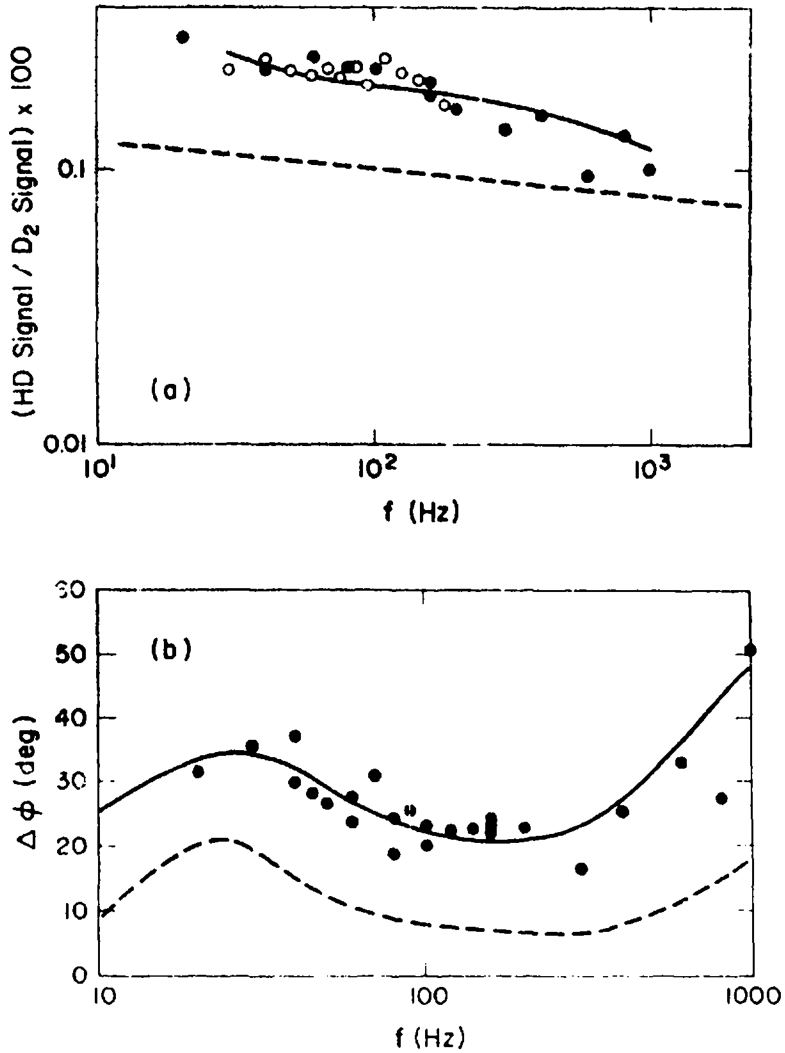


Fig. 4. (a) Relative HD amplitude and (b) HD phase-lag at 1000 K versus modulation frequency on Pt-S[9(111) × (111)]; (o) data of Bernasek and Somorjai; dashed line, analysis of B–S; solid line, this work. (The data points in this figure were plotted taking the data at 40 Hz of figs. 1 and 2 as locator points.)

respectively. For the Pt-S[9(111) × (111)] surface P_s was taken to be 0.28 (see curve a of fig. 1). This mechanism reproduced all of the experimental results quite well, including (1) the low apparent activation energy of 0.6 kcal/gmole above 600 K, (2) the phase reversal at high temperatures, and (3) the frequency dependence of the phase and amplitude. In addition, excellent agreement was obtained with the phase–temperature and amplitude temperature behavior observed at 160 Hz [3].

It is important to note that the difference in the frequency dependence of the phase and amplitude at the two different temperatures and, indeed, the phase reversal at temperatures above 600 K were consequences of the complex behavior of branched processes that arise in MBRS. In order to distinguish between a branched process and a simple first-order process, the ratio of rate constants k_s/k_t must be five or greater [4]. According to our mechanism, at 485 K the ratio was roughly two, whereas at 1000 K the ratio increased to 7.6. Thus at 485 K the reaction exhibited apparent simple first-order behavior, whereas at 1000 K the sluggish response of the phase and amplitude with changing frequency characteristic of branched processes appeared. Further, no change in mechanism occurred at 600 K; the observed behavior was the result of the admixed temperature-dependence of the two rate constants.

Our mechanism predicted the trend in experimental results on the Pt-S[5(111) × (111)] surface if the branching probability, P_s, was increased to 0.43 to account for higher step densities. It is important to note that *the total reaction probability was not changed*, a higher fraction of the exchange reaction took place on the steps as the step density was increased. Since an increase in P_s was associated with higher step density, it seems reasonable to associate the rate constant k_s with surface atoms of lower coordination number on the stepped surfaces. Further as shown in fig. 2, if the amplitude calculated for the reaction on the Pt-S[5(111) × (111)] surface was multiplied by 1.30 the experimental data was fit quite well. Thus, the *total* reaction probabilities on these two surfaces differed by no more than 30%. It should be noted that the temperature dependence of the phase-lag was also represented well by the simple branched mechanism with a step-density-sensitive branching probability.

The reinterpretation of the mechanism of the exchange reaction also suggests that the actual exchange probability on stepped surfaces may not differ as greatly from "non-stepped" surfaces as presently believed. AC amplitudes at 400 Hz at a surface temperature of 1000 K were utilized to calculate exchange probabilities of 1×10^{-6} for non-stepped Pt(111), 4.9×10^{-4} on Pt-S[9(111) × (111)], and 9.2×10^{-4} for the Pt-S[5(111) × (111)] surface [1]. At 400 Hz and 1000 K, however, the values of ω/k_s and ω/k_t were 4.3 and 32.0, respectively. Any amplitude response due to reaction on the terraces was thus strongly demodulated, see eq. (1). Evidence for the selective demodulation of the reaction on the smooth (111) plane was indeed observed when the modulation frequency was reduced to 40 Hz, and the reactant pressure was increased ten-fold; under these conditions the reaction probability for the smooth Pt(111) surface increased by a factor of 30 while that for the stepped surfaces increased by about six. These reported reaction probabilities must therefore be viewed as apparent values; the true values must be obtained in the limit of ω/k approaching zero

We estimated the ratio of reaction probabilities on the stepped surface and the smooth Pt(111) surface to be 18 using our mechanism and rate constants and the ac amplitudes measured by Bernasek and Somorjai at 40 Hz. Correcting the 400 Hz amplitude values to 40 Hz gave apparent amplitudes of 3×10^{-5} and 3×10^{-3}, respectively, as discussed above. Thus, the ratio of amplitudes for stepped [Pt(997)] and unstepped [Pt(111)] surfaces was 100. The relative *total* reaction probability on the two surfaces was estimated as follows.

The ac amplitude, A, for the reaction product is given by [4,6]

$$A = S_0 I_0 / \sqrt{1 + (\omega/k)^2}\,, \tag{1}$$

where S_0 denotes the reaction probability, I_0 denotes the *incident* reactant flux, and ω is the modulation frequency. *If the surface reaction can be considered second order* [2], in linearized form

$$k = 2\sqrt{S_0 I_0 k_2}\,, \tag{2}$$

where k_2 is the true second order rate constant [5,6]. Taking the apparent rate constants calculated for the branched mechanism on the stepped surface, Pt(997), $A_{(997)} = 0.40\, S_{(997)} I_0$. For the non-stepped, Pt(111), surface

$$A_{(111)} = \frac{S_{(111)} I_0}{\sqrt{\{1 + [\omega / 2\sqrt{S_{(111)} I_0 k_{2,(111)}}]^2\}}}\,. \tag{3}$$

If $k_{2,(111)}$ is identified with reaction on the (111) terraces alone, $k_{2,(111)} = k_{2,t}$. Since $(\omega/k_t)^2 >> 1$, eq. (3) simplifies to

$$A_{(111)} = \frac{S_{(111)} I_0\; 2\sqrt{S_{(111)} I_0 k_{2,t}}}{\omega}\,. \tag{4}$$

The effective rate constant k_t was evaluated on the *stepped* (997) surface, and was therefore related to $k_{2,t}$ by the expression

$$k_t = 2\sqrt{S_{(997)} I_0 k_{2,t}}\,. \tag{5}$$

Note that $S_{(997)}$ must be employed in the evaluation for k_t. It is easily seen that

$$\frac{A_{(997)}}{A_{(111)}} = 0.40\, \frac{\omega}{k_t} \left(\frac{S_{(997)}}{S_{(111)}} \right)^{3/2}\,, \tag{6}$$

since the amplitudes are compared at identical reactant fluxes. The ratio of the total reaction probabilities $S_{(997)}/S_{(111)}$, at 1000 K on these surfaces was calculated to be 18. The differences in initial sticking probability of H_2 on Pt(110), (211), (100) and (111) observed by Lu and Rye varied by a factor of 20. Since the experiments of Somorjai and Bernasek were performed under conditions in which they effectively compared the sticking probability of D_2 on the various surfaces (when demodulation factors are accounted for), these are the appropriate results of Lu and Rye to which to compare their results. The above analysis indicates that the dependence of the probability of dissociative adsorption of hydrogen on surface crystallography measured by Lu and Rye and Bernasek and Somorjai is in close agreement.

It should be noted that the above mechanistic analysis does not by itself determine the reaction order nor specify the sites at which exchange takes place. Subsequent to adsorption the faster process in the parallel mechanism, k_s, is associated with a higher activation energy and a higher preexponential factor than that of the slower branch, k_t; the relative rates are thus largely governed by entropy effects in the transition state. In keeping with the assumed second-order kinetics, it does seem reasonable to associate the branch having higher activation energy and preexponential factor with a two-center reaction involving at least one atom bound more strongly at platinum surface atoms of lower coordination number such as those bound at step positions rather than on a perfect (111) plane. It is also important to note that the actual activation energies for the second-order rate constants, calculated to be k_s and k_t, were calculated to be 10.4 kcal/gmole and 5.4 kcal/gmole, respectively, see eq. (2).

In conclusion, our calculations show that H_2–D_2 exchange on stepped platinum surfaces may proceed via a simple parallel reaction with a branching probability dependent on step density. Further, though the final definitive experiments on the effects of steps on reaction probability may remain to be done, this analysis offers a testable alternative to that previously proposed, wherein the crystallographic effects on the sticking probability of H_2 on platinum and the effects of steps on the H_2–D_2 exchange probability appear to be of the same magnitude.

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