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Hot-complex-mediated abstraction and desorption of D adatoms by H on Si(100)

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The collision-induced associative desorption (CID) and abstraction (ABS) of D adatoms by H have been studied on the Si(100) surfaces. D$_2$ CID exhibits a feature common to that of a thermal desorption from a dideuteride phase. HD ABS proceeds along an apparently second-order kinetics rather than a first-order kinetics with respect to surface D coverages. The ABS cross section is about 6 Å$^2$, extremely large compared to the theoretical values. Both of the direct Eley-Rideal mechanism and the hot-atom mechanism are ruled out. A hot-complex-mediated reaction model is proposed for ABS and CID.

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The gaseous hydrogen atoms abstract hydrogen adatoms on Si(100) surfaces. The recent kinetic experiments in the reaction system H$^+$+Si/Ph/Si(100) revealed that in addition to abstraction (ABS) of surface adatoms D$_{ad}$ to form HD, collision-induced associative desorption (CID) of D$_{ad}$, i.e., H$^+$D$_{ad}$--D$_2$, also occurs. The kinetic mechanisms so far proposed for ABS and CID reactions are still controversial. Dinger, Lutterloh, and Kippers insist on a so-called hot-atom (HA) mechanism rather than a direct Eley-Rideal (ER) mechanism for both ABS and CID. The HA scenario claims that incident H atoms first weakly chemisorb to the surface retaining the adsorption energy and go across the corrugated potential barriers as hot precursors H* for the abstraction of D$_{ad}$. The incident H atoms may generate secondary hot D* atoms that also abstract D$_{ad}$ to form D$_2$. Therefore, the HA scenario claims a first- and a second-order kinetics for ABS and CID, respectively, with respect to D$_{ad}$ coverage $\theta_D$. Dinger, Lutterloh, and Kippers deduced the second-order kinetics for D$_2$ CID by comparing the slopes of exponentially decaying HD and D$_2$ rate curves measured as a function of H admission time.

On the other hand, Shimokawa et al. observe that the reaction order of D$_2$ CID is approximately four with respect to $\theta_D$, indicating that four adatoms take part in the D$_2$ desorption process. The fourth-order kinetics in $\theta_D$ is quite unexpected, which rules out the HA mechanism. Earlier to this study, Flowers et al. admitted that the observed H and D uptake curves are not fit to a Kisliuk model, indicating that such a HA mechanism is not operative even for ABS as well. They proposed a thermodynamically quasi-equilibrium rate theory that includes not only an ER ABS but also an efficient sticking of H to the terminated Si(100) surface to form transient dideuterides DSiD. The dideuterides were considered to generate D$_2$ desorption along the same mechanism as for the so-called $\beta_3$ TPD (temperature-programmed desorption) arising from a dideuteride phase. The nearly fourth-order kinetics in $\theta_D$ observed for D$_2$ CID is not at variance with the Flowers model since the $\beta_2$ TPD obeys a second-order kinetics with respect to DSiD coverages involving four D$_{ad}$ in the event. Thus, CID based on the $\beta_2$ TPD mechanism is categorized as a Langmuir-Hinshelwood (LH) reaction. HD CID is also expected to take place in the H and D coadsorption system generated by substitution of D$_{ad}$ with H$_{ad}$ during H admission. Actually, the observed HD rate curves exhibit a bimodal structure particularly at small initial D coverages $\theta^0_D$, suggesting the occurrence of two distinct channels, i.e., HD CID along the LH mechanism and ABS via the direct ER mechanism. Khanom et al. propose a HD rate equation to fit to the experimental data obtained for $\theta^0_D=1.0$ ML (ML: monolayer, one D atom per surface Si atom),

$$\frac{dN_{HD}}{dt} = k_{ABS} \theta_{DD} + C_1 \theta_{HD} \theta_{DD} + 2C_2 \theta_{HD} \theta_{HD} + C_3 \theta_{HD} \theta_{HH},$$

where $k_{ABS}$ is the rate constant for the ER type ABS, and $C_n$ ($n = 1 \sim 3$) stands for the rate constants related to the three possible combinations of dideuterides upon their encounters for the LH type CID. For the CID terms in Eq. (1), the coverages of D$_{ad}$ in the prepared Si dimer, $\theta_{ij}$ ($i,j = H,D$), are employed instead of the unmeasured transient dideuteride coverages. Even for the ABS term $\theta_{DD}$ is taken instead of $\theta_D$ ($= \theta_{DD} + \theta_{DH}$). This means that in the viewpoint of ER scenarios for ABS, H abstracts D$_{ad}$ preferentially in the doubly occupied Si dimers DSi-SiD rather than D$_{ad}$ in DSi-SiH. Yet, the significance of this unexpected isotope effect on ABS has not been clarified.

In the two papers, however, the experiments were carried out at a fixed temperature around 600 K without systematic changes of $T_s$. If ABS and CID proceed along the HA scenario, it can be anticipated that they commonly receive a little $T_s$ effect. It is thus a dilemma for Dinger et al. to see a somewhat strong $T_s$ dependence on CID studied on Si(111). On the contrary, the CID model based on the LH mechanism predicts a strong $T_s$ dependence as was partly exemplified on Ge(100). In this paper, by examining $T_s$ effects on ABS and CID, we reveal their kinetic mechanisms on Si(100), and propose a hot-complex-mediated reaction model.

The details of the experimental method have been given previously. Here, the essential points are described briefly. The H(D) beams were obtained from a plasma of H$_2$(D$_2$)/Ar
mixed gas. The base pressure of a reaction chamber was 8 \times 10^{-11}\text{Torr}, while it was 6 \times 10^{-10}\text{Torr} under the beam admission. The flux of H and D beams was evaluated to be 6.5 \times 10^{12}\text{cm}^2\text{s}^{-1} at the surface. After saturating the Si(100) surface with 1 ML D atoms at 600 K, the H beam was admitted to the Si(100) surface to induce desorption of HD and D$_2$ at various surface temperatures ranging from 300 to 700 K. The quick temperature rise from 600 K to desired temperatures for $T_s > 600$ K was accomplished within a few seconds by means of a direct resistive heating.

During H admission to the D/Si(100) surface, HD and D$_2$ molecules were detected with a quadrupole mass spectrometer (QMS), while we failed to detect H$_2$ because of background H$_2$. Spontaneous thermal desorption of D$_2$ already started before H admission above 600 K, and thus the D$_2$ rates at $t = 0$ can be decomposed into CID (solid rectangles) and spontaneous thermal desorption (STD) (solid circles) as shown in the inset of Fig. 1. Plots of D$_2$ rates normalized with the initial HD rate $[I_0(D_2)/I_0(\text{HD})]$ versus $T_s$ are shown in Fig. 1. The D$_2$ CID curve exhibits a clear peak around 590 K above which the D$_2$ CID rates decrease quite rapidly in spite of the sizable amount of residual D$_{ad}$ at the beginning of H admission (the loss of D$_{ad}$ before H admission was at most 0.15 ML at $T_s = 683$ K). On the other hand, STD begins to appear around 600 K and increases quite rapidly with $T_s$. For comparison, we plot decomposed $\beta_2$ and $\beta_1$ TPD spectra arising from the dideuteride and monodeuteride phase, respectively. The STD spectrum exhibits a close relation to the $\beta_1$ TPD spectrum, which was expected since it occurs from the monodeuteride phase. On the other hand, the D$_2$ CID spectrum looks similar in line shape to the $\beta_2$ TPD spectrum.

The feature of the CID and STD rate spectra manifests an anticorrelation for $T_s > 600$ K, indicating the former succumbs to the latter at higher $T_s$. From $I_0(D_2)/I_0(\text{HD}) = 0.23$ at 590 K, we know that about one third of the desorbed D atoms were due to CID on the H$_{ad}$ free D/Si(100) surface.

Reaction orders for the D$_2$ desorptions were evaluated by fitting the experimental rate curves to a rate equation, $\frac{dN_{D_2}}{dt} = k\theta_D^m$, that consists of a single term characterized with the rate constant $k$ and the reaction order $m$. However, the actual rates may include not only multiterms of CID as in Eq. (1) but also a term of STD, and the evaluated reaction orders are thus apparent. Figure 2 shows a plot of the D$_2$ CID reaction orders so determined as a function of $T_s$. The inset shows the curve fittings based on a least mean-squares method for $T_s = 300, 593$, and 683 K. Here, the momentary D$_{ad}$ coverages $\theta_D$ during H admission were obtained by integrating the HD and D$_2$ rate curves.$^{7,15}$ The reaction orders for D$_2$ CID were evaluated to be $3.7 \pm 0.3$ for the temperature range from 500 to 600 K where the CID rates are high but the STD rates are low, indicating that D$_2$ CID proceeds along a nearly fourth-order kinetics in $\theta_D$ as noted previously for $T_s = 573$ K.$^7$ The fourth-order kinetics rules out the HA mechanism for D$_2$ CID. It is also ruled out even at $T_s = 300$ K because the observed reaction order is about six.

From the facts shown in Figs. 1 and 2, we conclude that D$_2$ CID on Si(100) proceeds along the same mechanism as for the $\beta_2$ TPD arising from the dideuteride phase. In other words, the DSiD species are formed by H on the D/Si(100) surface, however, transiently since $T_s$ is so high that they do not steadily survive. The second-order kinetics with respect...
The HD rate is clearly lower than the line for \( \theta_D = 0.85 \) ML, after which the HD rate curve shows a tiny peak around 0.1 ML, before decreasing with decreasing \( \theta_D \). Therefore, we conclude that neither the HA mechanism nor the direct ER one are operative for the D ad abstraction by H because the two mechanisms commonly claim a first-order kinetics in \( \theta_D \). Besides, taking into account the feature that the ABS rate curve is a simply decreasing function with decreasing \( \theta_D \) on the saturated surface, the maximum in the HD rate around \( \theta_D = 0.85 \) ML is attributed to HD CID overlapping ABS. With the light of the present results and the rate-curve analysis done at \( T_s = 573 \) K,\textsuperscript{14} we confirm that Eq. (1) and the physics and chemistry behind it are valid. Since the relation that \( \theta_{ij} = \theta_\theta \theta_\theta \) (\( i,j = D, H \)) is held on the surface saturated with randomly mixed \( H_{ad} \) and \( D_{ad} \),\textsuperscript{14} the ABS term in Eq. (1) can be recast as \( (dN_{HD}/dt)_{ABS} = k_{ABS} \theta_\theta^2 \). Thus, the HD ABS reaction on the saturated Si(100) surface follows an apparently second-order kinetics in \( \theta_D \). Using the relation that \( \theta_D + \theta_H = 1 \) during H admission,\textsuperscript{3} Eq. (1) is recast as a function of \( \theta_D \) (see the figure caption), and the HD rate curve is decomposed into ABS and CID as shown in Fig. 3. We notice that the rates for both ABS and CID are comparable after the middle stages of H admission.

Taking into account the balance between the uptake on and loss from the surface keeping the 1 ML saturation coverage, we can evaluate ABS efficiency \( \xi \) at \( t = 0 \) as \( \xi = I_0(HD)/(2I_0(HD) + 2I_0(D_2) + I_{rot}) \) for \( T_s \approx 600 \) K. Here, \( I_0(HD) \) and \( I_0(D_2) \) are the initial HD and D\(_2\) rates, respectively, and \( I_{rot} \) is the reflected H flux. Taking the reflection probability of 0.05 as evaluated theoretically by Hansen and Vogl,\textsuperscript{16} and employing \( I_0(D_2)/I_0(HD) = 0.23 \) for \( T_s = 593 \) K as plotted in Fig. 1, we obtain \( \xi = 0.39 \). This value corresponds to a sticking probability \( s = 0.56 \), and yields an abstraction cross section \( \sigma = 6 \) Å\(^2\) as evaluated from the relation \( \sigma = \xi/3 \) (\( 5 \times 1 \times 1 \) unit cell area). This is extremely large compared to the size of a hydrogen molecule. According to the recent quantum-mechanical calculations based on a flat surface model avoiding sticking,\textsuperscript{17} cross sections of the direct ER abstraction, \( \sigma_{ER} \), becomes small with increasing H-substrate binding energy \( E_B \). For \( E_B = 3 \) eV, close to the value \( E_B = 3.4 \) eV on Si,\textsuperscript{18} it has been estimated that \( 6 \times 10^{-5} \leq \sigma_{ER} \leq 0.025 \) Å\(^2\). Therefore, there exists a serious discrepancy between the theory and the experiment on the ABS cross sections.

Since it was observed in this work that the ABS reaction is neither of a direct ER type nor of a HA one, a new model for the ABS mechanism is needed to solve the ABS puzzle, i.e., the large cross section and the apparently second-order kinetics for ABS. We seek a hint in the high reactivity of H with the substrate, since the formation of dideuterides is quite facile on Si(100) as confirmed by the \( \beta_2 \) TPD. In other words, the sticking probability of H to the D/Si(100) surface is much larger than that of the direct ER type ABS. The classical molecular-dynamics simulation\textsuperscript{16} in the same system showed that in addition to the high ABS probability of about 0.4 the adsorption probability of H is as high as 0.6. Although the adsorption in the simulation does not necessarily mean dihydrides, the simulated feature of the H reaction with D\(_{ad}\) is thus quite close to the present results. Such high reaction probability may be assured by three mechanisms: (1) the potential felt by the incident H is attractive on almost the entire surface, (2) the corrugation of this potential prolongs the interaction time and confines the event locally, and (3) the efficient momentum and energy transfer take place to the Si lattice as well as to the adsorbates. If we look at this

\[ H(g)+D/Si(100) \rightarrow HD \]

**Fig. 3.** Plots of HD rate curves measured at \( T_s = 593 \) K and 300 K (inset) as a function of \( \theta_D \). The dashed line (a) shows the first-order kinetics with respect to \( \theta_D \) expected in the direct ER or HA scenario. The experimental rate curve is fit to the rate equation, \( dN_{HD}/dt = k_{ABS} \theta_\theta^2 + C_1 \theta_\theta \theta_\theta^2 + C_2 \theta_\theta^2 \theta_\theta + C_3 \theta_\theta \theta_\theta \), which is derived from Eq. (1) in the text after taking \( \theta_{ij} = \theta_\theta \theta_\theta \) for \( i,j = H, D \). For \( \theta_{i=0} + \theta_{j=0} = 1 \), the best fit curve [A] is obtained for the rate constants, \( k_{ABS} = 1.35 \times 10^{-3} \) s\(^{-1}\) [curve (b)], \( C_1 = 5.2 \times 10^{-3} \) ML\(^{-1}\) s\(^{-1}\) [curve (c)], and \( C_2 = 0.27 \times 10^{-3} \) ML\(^{-1}\) s\(^{-1}\) [curve (d)]. The third term of CID is negligibly small.
feature from a quantum-mechanical point of view, the chemisorbed hydrogen before full relaxation is in vibrationally excited states rather than in free conduction-band states. Here, such a vibrationally excited H-chemisorbed system is called a hot complex, and is invoked to explain a new mechanism for ABS other than an ER mechanism and a HA one. The following is proposed as a new mechanism of hot-complex-mediated ABS and CID on Si(100): Major fractions of incident H atoms first get trapped in the chemisorption potential not as a hot atom H* but as a hot complex (H+DSi-SiD)*, where based on the fact that \( \frac{dn_{\text{HD}}}{dt}_{\text{ABS}} \approx k_{\text{ABS}} \theta_{DD} \) in Eq. (1), the doubly occupied Si dimers DSi-SiD (including DSi-SiH and HSi-SiH for \( t>0 \)) is chosen as a skeleton of the complex. This hot complex does not allow us to release the H atom into the mobile states or H*. The generation of ABS and formation of HSiD take place from the hot complex competitively:

\[
H + \text{DSi-SiD} \rightarrow (H + \text{DSi-SiD})* \rightarrow \text{HD+Si-D,} \quad (2) \\
\text{HSi+SD.} \quad (3)
\]

The exothermicities of the relevant reactions are evaluated to be \(-1.1\) and \(-2.6\) eV for Eqs. (2) and (3), respectively, for the bond energies of HD (4.5 eV), H-Si (3.4 eV, Ref. 18) and Si-Si dimer (1.9 eV, Ref. 19). Therefore, the HSiD formation is facile compared to ABS, which is not at variance with the experiment. The HSiD species formed along Eq. (3) are precursors for CID that subsequently proceeds along the same mechanism as for the \( \beta_2 \) TPD.\(^{13} \) Hence, the HD desorptions consist of ABS via Eq. (2) and CID initiated by HSiD formed via Eq. (3). The HD desorption via Eq. (2) is a non-thermal process and thus expected to show a dynamic feature\(^{5}\) similar to those theoretically predicted in the ER and HA scenarios.\(^{10,20} \) The fate of the hot complex either to ABS or to dihydride followed by CID may be determined by potential-energy surfaces at impact sites, phases of vibrations relevant to reaction coordinates, mass of the adatoms, etc. A hot complex (H+HSi-SiD)* arising from H sticking to HSi-SiD has a chance to generate either H\(_2\) ABS or formation of HSiH, competing with HD ABS and formation of HSiD. This competition could cause the less efficient HD ABS at the late stages of H admission. In the ER scenario, the isotope effect on ABS is interpreted in terms of kinematics upon collision.\(^{10,21,22} \) In the present hot-complex model, it is explicable in terms of quantum effects upon relaxation of the hot complex, including a zero-point vibrational energy effect, an attempting frequency factor to transition states, tunneling through barriers, etc. Generally speaking, lighter atoms are superior to heavier ones in such quantum-mechanical transitions. Therefore, the preferential D\(_{\text{ad}}\) abstraction from DSi-SiD rather than from DSi-SiH, i.e., the first term in Eq. (1), could be reconciled with such quantum effects on the reaction in the hot complex.

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