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Surface Science

Adsorbate Alignment in Surface Halogenation: Standing Up is Better than Lying Down**

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Almost half a century ago, it was demonstrated that an aligned gaseous reagent molecule had a reactivity for abstractive halogen-atom transfer that depended on the direction of approach of the alkali metal atom that abstracted the halogen.[1] At surfaces, adsorbates are commonly aligned,[2] offering opportunities to examine the effect of molecular alignment on surface reaction. Molecules usually adsorb in a horizontal (*h*) state at low coverages, maximizing their interaction with the underlying surface, and in more-nearly vertical (*v*) states at increased coverages.[3] Recently, Dougherty et al.[4] noted a change in electronic properties between "standing-up" (*v*) and "lying-down" (*h*) pyridine on Cu(110).

Studies in this laboratory of the adsorption and reaction of haloaromatics[5] and haloalkanes[6] at silicon surfaces, using scanning tunneling microscopy (STM), provided evidence of vertical, *v*, and horizontal, *h*, states of single adsorbates at Si(111)-7 × 7; examples being 1-bromopropane,[6a,b] 1-bromopentane,[6c] 1-chlorododecane,[6d–f] and 1-bromododecane.[6e,f] Experimentally, the assignment of adsorbate alignment (*v* vs *h*) is based on contrasting surface mobilities[6a–f] (*v* more mobile than *h*) and sometimes differing STM imaging[6a–c] (*v* higher than *h*). The ratio of *v* to *h* varied with deposition rate[6c,f] and surface temperature.[6f,7]

Both reactive pathway and reaction rate are different for *v* and *h* states. (We earlier referred to *v* reaction as "daughter-mediated"[5b,c,6a,d–f] or "direct",[8] *h* reaction as "parent-mediated"[5b,c,6a,d–f] or "indirect".[8]) The *v* reaction path frequently resulted in only the halogen-atom bound to the surface, whereas *h* occasionally gave halogen-atom and organic radical both bound to the surface.[6e,f]

For 1-bromododecane on Si(111)-7 × 7,[6f] measurements of thermal reaction showed *v* reacted more rapidly than *h*, in qualitative accord with the computation of the thermal reaction of CH_3Br brominating the same Si(111)-7 × 7 surface[9] which showed horizontal (*h*) physisorbed CH_3Br converting to a more-nearly *v* configuration during the approach to the transition state. A requirement that *h* adsorbate "stand-up" (*v*) en route to the transition state was apparent for a series of 1-bromoalkanes reacting by dissociative attachment on Si(100)-c(4×2); the activation energy for bromination increased with alkyl chain length in parallel with the computed energy required to go from *h* to *v*.[10]

Herein we use STM to identify the *v* and *h* states of 1-bromoalkanes with different alkyl chain lengths, 1-bromopropane (PrBr) and 1-bromopentane (PeBr), on Si(111)-7 × 7. The *v*-states have higher mobility and greater height in STM topographs (Supporting Information, Figure S3). For PrBr and PeBr, we measured the rates of thermal reaction for *v* and *h*. For PeBr, we calculate, ab initio, adsorptions and reactions for both *v* and *h*, explaining the enhanced reactivity for *v* compared with *h*.

Qualitatively the explanation accords with our earlier rationale. The freedom of movement for *v* (as compared with *h*, bound by its alkyl chain to the surface) permits it to achieve the most favorable C–Br–Si alignment and Br–Si separation for reaction.[6f] Early experiments indicated that the optimal alignment for the C–Br bond being broken and the Br–Si bond being formed was collinear, permitting a vectorial description of the dynamics.[5a,b] A priori calculation for two separate examples (one earlier,[9] and one given herein), referenced in the theory part of the present work, support the requirement for near-collinearity in the transition state between the bond broken and that formed, that is, in C–Br–Si. We also find the Br–Si separation in the transition state has the bromine atom in the adsorbate proximal to its final Br–Si bonding distance. This required alignment and proximity is more readily achieved by the mobile *v*.

We also report energy thresholds and yields for the electron-induced reaction of the *v* and *h* states of PrBr and PeBr on Si(111)-7 × 7. For both PrBr and PeBr, the threshold voltage for *v* is about +1 V less than for *h*, while electron yields for *v* were about 1000 × greater than for *h*. The resemblance of this finding for relative reactivity of *v* and *h* in electron-induced reaction to that obtained for *v* and *h* in thermal reaction (as noted in our earlier work[9,11]) would be understandable if in the electron-induced reaction the system returned rapidly to the ground electronic state encountering a similar energy barrier on the ground potential-energy surface as in thermal reaction. The difference in electron yield suggests an enhanced transition probability to the anionic

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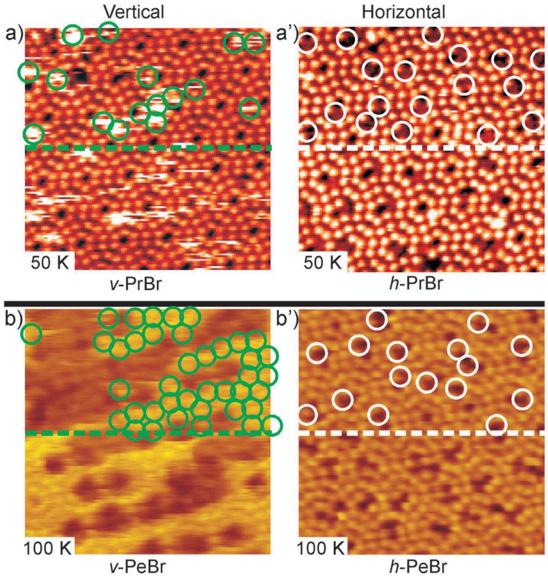

Figure 1. Physisorption of 1-bromopropane (PrBr) and 1-bromopentane (PeBr) in vertical and horizontal states. The left column shows the vertical states for a) *v*-PrBr at 50 K and b) *v*-PeBr at 100 K. The right column shows the horizontal states for a′) *h*-PrBr at 50 K and b′) *h*-PeBr at 100 K. In the top half of all panels, the physisorbed 1-bromoalkanes are indicated by circles. All images are about 140×140 Å^2 in size. Imaging conditions: $V_{\text{sample}} = +1.5$ V and $I = 0.2$ nA for (a), (a′), and (b′); $V_{\text{sample}} = +1.0$ V and $I = 0.2$ nA for (b).

state for vertical adsorbate, recalling the effect of adsorbate alignment on adsorbate electronic properties observed by Dougherty et al.[4])

Figure 1 shows the vertical (at left) and horizontal (at right) physisorbed states of PrBr and PeBr. Both *v* and *h* coexist on Si(111)-7×7: at 50 K for PrBr and at 100 K for PeBr. We assigned the two observed states for PrBr and PeBr to *v* and *h* (as for earlier work[6]) by their surface mobilities and STM image heights, in agreement with our ab initio calculations given below. The mobile *v* molecules show some aggregation at 50 K (see Figure 1a for PrBr) and islanding at 100 K (see Figure 1b for PeBr). At lower coverages, Figure 2a, groups of three *v* molecules were commonly found.

Thermal reaction of PrBr and PeBr on Si(111)-7×7 was studied at surface temperatures between 100–160 K; rates for both *v* and *h* configurations of PrBr and PeBr were measured separately, leading to values for the energy barriers $E_a(v)$ and $E_a(h)$. Numbers of bromine atoms formed from the precursors were recorded at various times for a statistically meaningful sample of molecules. To eliminate tip-induced effects,[12] measurements were made at uneven time intervals using imaging biases ($\leq +1.5$ V) below the threshold voltages for electron-induced reaction (see the Supporting Information).

Examples of thermal rate measurements of PeBr on Si(111)-7×7 are given in Figure 2. Figure 2a and b show the thermal reaction for v-PeBr at 100 K. After 2 min, three *v*-PeBr molecules (imaged bright, circled in Figure 2a), had reacted to form bromine atoms (imaged dark, circled in Figure 2b). Similarly, Figure 2c and d show the thermal reaction for *h*-PeBr at 160 K. After 21 min, four *h*-PeBr molecules (imaged dark, circled in Figure 2c), had reacted to form bromine atoms (imaged bright, circled in Figure 2d). During our thermal rate measurement of PeBr, we observed a total of 110 reactive events for *v* over about 13 min at 100 K, and 22 reactive events for *h* over about 21 min at 160 K.

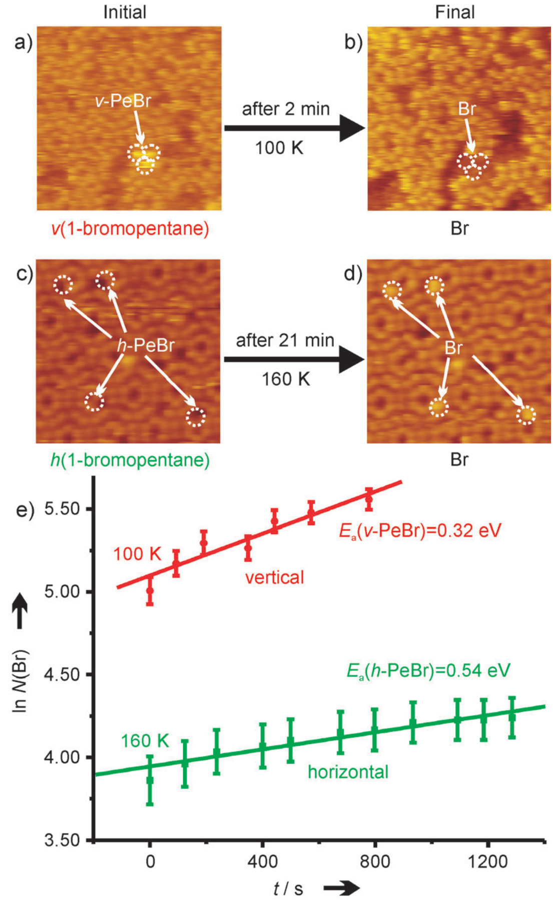

Figure 2. Measurements of thermal reaction barriers for vertical and horizontal 1-bromopentane. Examples of reactions are given in a) and b) for *v*, and in c) and d) for *h*. e) The logarithm of surface bromine atom numbers against time (experimental uncertainties shown are the square-root of the count) giving thermal barriers as $E_a(v\text{-PeBr}) = 0.32$ eV and $E_a(h\text{-PeBr}) = 0.54$ eV. All images are about 127×127 Å^2, obtained with $I = 0.2$ nA; $V_{\text{sample}} = +1.5$ V for (a) and (b); $V_{\text{sample}} = +1.4$ V for (c) and (d).

The products of thermal reaction are chemisorbed bromine atoms, identified by the characteristic lighting-up at a sample bias between +1.0 V and +2.5 V,[5a] and confirmed by the thermal stability of the features for days at 300 K, in contrast to the spontaneous dissociation[6b] of physisorbed PeBr at the same temperature. Product bromine atoms exclusively chemisorbed at the prior physisorption sites, as shown in Figure 2a–d. This is a localized atomic reaction (LAR),[13] a concerted process documented[9] for semiconductor[5,6,9–11,13–15] and metal[16,17] surfaces.

In no case, *v* or *h*, did alkyl radicals attach to Si(111)-7×7, implying that the transition state geometries favor the ejection of the alkyl radical. The abstraction of halogen atoms from physisorbed haloalkanes was previously observed on Si(111)-7×7[6,9] without corresponding alkyl attachment.

This is consistent with a transition state in which, even for horizontal adsorbates, the alkyl group is distant from the surface (see below). The exceptions were 1-chlorododecane and 1-bromododecane for which the horizontal state occasionally gave alkyl attachment to the surface.[6e,f] These dynamics on Si(111) contrast with the dissociative attachment on Si(100), where both the halogen atoms and the alkyl groups were invariably found bound to the surface.[10,18] No *v* to *h* conversions were observed in our extensive measurements. We believe that this is due to predominance of surface bromination over *v* to *h* conversion.

To determine reaction rates, the logarithms of the number of bromine atoms, ln *N*(Br),[19] were plotted against elapsed time, for both vertical and horizontal states of physisorbed PeBr. The reaction rate data from different surface sites were first analyzed separately but were identical within errors. Subsequently, data from different surface sites was combined; fits of the combined data yield slopes, $k(v\text{-PeBr}) = (6.3 \pm 1.0) \times 10^{-4}\,\text{s}^{-1}$ and $k(h\text{-PeBr}) = (2.5 \pm 0.9) \times 10^{-4}\,\text{s}^{-1}$. Assuming a pre-factor of $10^{13}\,\text{s}^{-1}$ in the Arrhenius formula, we obtain the thermal barriers for PeBr on Si(111)-7 × 7 as $E_a(v\text{-PeBr}) = (0.32 \pm 0.01)$ eV and $E_a(h\text{-PeBr}) = (0.54 \pm 0.01)$ eV. Similarly, the thermal barriers for PrBr on Si(111)-7 × 7 were found as $E_a(v\text{-PrBr}) = (0.34 \pm 0.01)$ eV and $E_a(h\text{-PrBr}) = (0.46 \pm 0.01)$ eV. Only relative uncertainties from the fit have been quoted; we estimate the absolute uncertainty for thermal barriers as about 50 meV using $10^{13\pm2}\,\text{s}^{-1}$ for the pre-factor.[11] As it is relative energies that are of interest, and the systems being compared are all 1-bromalkanes on Si(111)-7 × 7, assuming the same pre-factor should be a good approximation.

We also measured (see the Supporting Information) the electron-induced reaction of both *v* and *h* physisorbed PrBr and PeBr on Si(111)-7 × 7. The electron-induced reaction is again bromine abstraction, not dissociative attachment, with *v* more reactive than *h*; the threshold voltages for *v* (for both PrBr and PeBr) were about +2 V, and those for *h* (for both PrBr and PeBr) were about +3 V. The measured electron yields were of 10^{-6}–10^{-7} per electron for *v* and 10^{-9}–10^{-10} per electron for *h*. The qualitative resemblance between electron-induced reaction and thermal reaction may be because in these electron-induced reactions the system returns promptly to the ground state, traversing a similar energy barrier to that for thermal reaction. We previously noted a similar parallelism for 1-chloropentane on Si(100)-2 × 1.[11]

Plane-wave-based ab initio calculations were employed to examine our main exemplar, PeBr on Si(111)-7 × 7, using the Vienna ab initio simulation package (VASP 5.2.11)[20] installed at the SciNet supercomputer[21] (see the Supporting Information). Figure 3 a and b show computed geometries for both physisorbed initial states, *v* and *h*, at the middle Si-atom of the faulted half-cell of Si(111)-7 × 7. The *v* (Figure 3 a) and *h* (Figure 3 b) states mainly differ in the alignment of the pentyl chain with respect to the surface. For both *v* and *h* initial states, the bromine atoms are close to the silicon adatom with a short Br–Si separation of 2.7–2.9 Å; this close separation is only 0.3–0.5 Å longer than the covalent Br–Si bond length of 2.29 Å,[22] in line with a dative bonding between the lone-pair bromine electrons and electrophilic silicon adatom. The C–Br separations of about 2.0 Å in both physisorbed states were essentially identical to those in the free molecules (1.93 Å).[22]

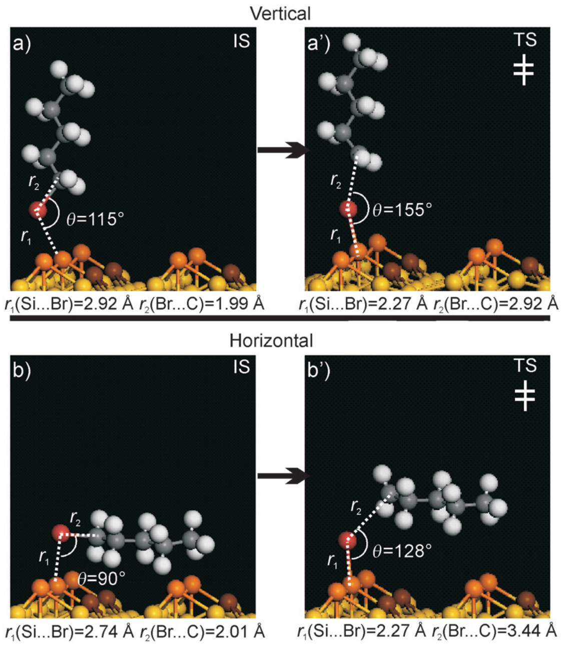

Figure 3. a), b) Computed initial state (IS) geometries of *v*-PeBr and *h*-PeBr on Si(111)-7 × 7. Corresponding transition state (TS) geometries for *v*-PeBr and *h*-PeBr are given in (a′) and (b′). The silicon adatoms are colored orange and silicon rest atoms are colored brown so as to be distinguishable from bulk silicon adatoms (colored yellow).

The physisorption energies for *v* and *h* states of PeBr were calculated as $E_{\text{ads}}(v\text{-PeBr}) = 0.20$ eV and $E_{\text{ads}}(h\text{-PeBr}) = 0.68$ eV, which is consistent with our observation of markedly greater mobility for *v* than *h* at 100 K. The lower physisorption energy for *v* than *h* presumably arises from the lesser van der Waals interaction between the pentyl chain and the surface; the *v*-PeBr attaches to the surface only via its bromine atom, whereas *h*-PeBr state is adsorbed at the surface along the full length of the pentyl chain. Similar geometries and energies of physisorption (ca. 0.2 eV for *v* and ca. 0.6 eV for *h*; see the Supporting Information) were computed at different sites of Si(111)-7 × 7; this result is not site-specific as was also found for reaction rates measured at different sites (see above).

The minimum energy pathways for the reactions of PeBr on Si(111)-7 × 7 were computed using the climbing image nudged elastic band (CI-NEB) technique,[23] which locates the transition states. As we have no evidence of site-specificity, we restricted our CI-NEB calculations for both *v* and *h* physisorbed states with the Br-atom above the middle silicon atom of the faulted half-cell of Si(111)-7 × 7. Pentyl radicals in final states were displaced vertically away the surface by about 6 Å (effectively in the gas phase). This definition of the final states is known[9,24] to lead to reasonable transition states in CI-NEB calculations for halogen abstraction reactions at silicon.

The computed transition states for both *v* and *h* are shown in Figure 3 a′ and b′. The C–Br separations in both transition states increase from those of initial physisorbed states (initial separation ca. 2.0 Å), to about 2.9 Å for *v* and to about 3.4 Å for *h*. Concurrently, the Br–Si separations in both transition states decrease from those of the initial physisorbed states (initial separation of 2.7–2.9 Å), to approximately the covalent Br-Si bond length of about 2.3 Å.[22] The activation energies were computed as E_c(*v*-PeBr) = 0.31 eV and E_c(*h*-PeBr) = 0.58 eV, in good agreement with the experimental values of E_a(*v*-PeBr) = (0.32 ± 0.01) eV and E_a(*h*-PeBr) = (0.54 ± 0.01) eV.

Comparing the computed initial and transition state geometries for *v* and *h* reveals the C–Br bond axis and the Br–Si bond axis (the bond being broken and that being formed) to be more-nearly collinear in the transition state than in the initial state (see introductory remarks). The same approach to collinearity in the transition state is evident in a previous ab initio calculation of C–Br–Si configurations in surface bromination; this was a study of the molecular dynamics in the reaction of CH_3Br on Si(111)-7 × 7.[9] As the silicon atom is fixed at the surface, C–Br–Si achieves collinearity by moving the carbon atom (upward in Figure 3) into line. As shown in Figure 3, for the vertical initial state, the upward motion of the carbon atom lifts the unattached pentyl chain, but for the horizontal initial state, the upward movement of the carbon atom in going to the transition state involves lifting the pentyl away from its adsorbed state at the surface. Accordingly, we ascribe the increased activation energy for surface bromination from the horizontal initial state, *h*, primarily to the work needed to lift the alkyl chain. The total desorption energy for the alkyl chain amounts to about 100 meV per CH_2 group. By contrast, the mobility of the vertical state, *v*, minimizes the work required to achieve the near-collinear C–Br–Si alignment.

The principal finding in this work, that vertical 1-bromoalkane adsorbates are more reactive than horizontal, may be general for surface halogenation, as it stems from the ease of formation of a near-collinear C–Br–Si transition state when the carbon atom is part of a mobile species *v* and, by contrast, the energy expended in raising the carbon atom toward C–Br–Si collinearity in the case of *h* in which an alkyl chain is initially attached to the surface. In Table 1, we assemble the available evidence regarding the measured thermal activation energies for both *v* and *h* states of four 1-bromoalkanes on Si(111)-7 × 7.[6f,9] The final column of the table demonstrates that the change in E_a is not due to alteration in the C–Br bond dissociation energy, D_e(C-Br, gas).[25] It appears from our results that the change in E_a with increasing chain length for *h* is due to the attraction between the alkyl chain and the surface, which increases with chain length.

Table 1: Comparison of measured activation energies for *v* and *h* states in the bromination of Si(111)-7 × 7.

Molecule	E_a [eV] (vertical)	E_a [eV] (horizontal)	D_e(C–Br, gas) [eV]
CH_3Br (MeBr)[a]	ca. 0.2[9]	ca. 0.2[9]	3.05[25]
1-C_3H_7Br (PrBr)	0.34	0.46	3.09[25]
1-$C_5H_{11}Br$ (PeBr)	0.32	0.54	3.06[25]
1-$C_{12}H_{25}Br$ (DoBr)	0.2[6f]	1.2[6f]	–

[a] This is based on our earlier experimental work,[9] which found a barrier of about 0.2 eV from different physisorbed states of CH_3Br on Si(111)-7 × 7.

As evident in Table 1 for a variety of 1-bromoalkanes on Si(111)-7 × 7, vertical physisorbed 1-bromoalkanes exhibit significantly lower activation energies for bromination reactions on Si(111)-7 × 7 than do their horizontal counterparts. The systematic increase in activation energy for surface bromination with the length of the alkyl chain in 1-bromoalkanes (for *h*) evident in Table 1 parallels observations made in this laboratory's recent study[10] of 1-bromoalkanes on Si(100)-c(4×2).

We have used STM to study the physisorption and subsequent bromination reactions of PrBr and PeBr on Si(111)-7 × 7. Two physisorbed states for each 1-bromoalkane, vertical (*v*) or horizontal (*h*), differing in the alignment of alkyl chain, were identified by STM. Reactivity was examined as a function of adsorbate alignment. For both thermal and electron-induced reactions, *v* was found to be more reactive than *h*. For thermal reaction, activation barriers for the vertical states were E_a(*v*-PrBr) = 0.34 eV and E_a(*v*-PeBr) = 0.32 eV, which are significantly less than those of their horizontal counterparts, E_a(*h*-PrBr) = 0.46 eV and E_a(*h*-PeBr) = 0.54 eV. For electron-induced reaction, the threshold voltage for *v* was about +1 V less than for *h*, and the electron yield for *v* was found to be about 1000 × greater than *h*.

We have used ab initio calculations to confirm the alternative physisorbed alignments, *v* and *h*, of the alkyl chain for the case of PeBr on Si(111)-7 × 7. Further, extensive ab initio calculations of the reaction of both *v* and *h* showed that the alignment of C–Br–Si approached linearity in the transition state (as pre-figured in our earlier study[9] of silicon bromination). This requires lifting of the alkyl chain, which involves the expenditure of energy in the case of the horizontally attached *h* conformer, increasing the energy required to reach the transition state. This provides a rationale for the lower energy barriers obtained for *v* compared to *h* in experiment and theory. As a similar systematic increase in activation energy for *h* with increasing alkyl chain length has now been observed on both Si(111)-7 × 7 and on Si(100)-c(4×2),[10] and as decreased adhesion of the alkyl chain to the surface appears to be responsible for the lower activation energy of *v* compared to *h*, we anticipate that the greater reactivity of *v* than *h* will extend to the reactions of other alkyl-chain molecules on other surfaces.

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