Dissociative adsorption of vinyl bromide on Si(001): A first-principles study

Jun-Hyung Cho
Department of Physics, Hanyang University, 17 Haengdang-Dong, Seongdong-Ku, Seoul 133-791, Korea

Leonard Kleinman
Department of Physics, University of Texas, Austin, Texas 78712-1081, USA

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The adsorption of vinyl bromide on the Si(001) surface is investigated by first-principles density-functional calculations within the generalized gradient approximation. We find that the formation of the two adsorption configurations (i.e., the di-σ structure on top of a Si dimer and the end-bridge structure across the ends of two adjacent Si dimers) takes place with no barrier. Both chemisorption states proceed to undergo C—Br dissociation over an energy barrier of ~0.30 eV. Our results do not support the conclusion drawn from a recent high-resolution electron energy loss spectroscopy (HREELS), where the formation of the di-σ structure would occur via a strongly bound precursor state with an activation energy of 0.283 eV. Our calculated energy profiles for the reaction pathways indicate that the precursor and chemisorption states proposed by the HREELS experiment should be reinterpreted in terms of the chemisorption and dissociative states, respectively.

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I. INTRODUCTION

The reaction of unsaturated hydrocarbon molecules with the Si(001) surface is of considerable interest because of its potential in technological applications such as nonlinear optical devices, chemical sensors, and molecular electronic devices.[1,2] A number of previous works[3–8] have established that unsaturated hydrocarbons containing a C═C double or a C≡C triple bond (e.g., acetylene,[3,4] ethylene,[5] cyclopentene,[6] 1,4-cyclohexadiene,[7] etc.) are attached to Si(001) through the so-called [2+2] cycloaddition reaction, where the π bond of the unsaturated hydrocarbon interacts with the π bond of the Si dimer, forming a four-membered ring with two new Si—C σ bonds. Such a [2+2] reaction on Si(001) has been observed to be facile at room temperature with a sticking coefficient of nearly 1.[5,9–11] This fact can be explained by the existence of a low-symmetry intermediate state along the reaction pathway, caused by the buckled Si dimer structure.[3,4,12] Note that there are two models for the intermediate state before formation of the [2+2] product.[3–5,12] One is a three-atom intermediate model [see Fig. 1(a)] which is composed of a three-membered ring with the two C atoms and the down atom of the Si dimer. The other is a diradical intermediate model [Fig. 1(b)] where the π bond of C═C is broken to create a single Si—C bond and a radical.

Using high-resolution electron-energy-loss spectroscopy (HREELS), Nagao *et al.*[13] studied the adsorption states of vinyl bromide (CH_2═CHBr) on Si(001). They observed an adsorption state at 58 K, which they proposed was a precursor before chemisorption. From the analysis of the vibrational spectra, Nagao *et al.* interpreted the precursor state in terms of the three-atom intermediate model. As the temperature increased to 90 K, Nagao *et al.* found that the three-atom intermediate state is transformed to a chemisorption state which was assigned to the di-σ structure [see Fig. 2(a)]. They also found that at 90 K, the dissociation of adsorbed vinyl bromide molecules occurs via C—Br bond cleavage, thereby leading to their conclusion that the di-σ bonded species and the dissociated CH_2—CH and Br species coexist at 90 K. By measuring the time-dependent HREELS spectra at a constant temperature between 83 and 90 K, Nagao *et al.* determined that the preexponential factor of the [2+2] reaction from the precursor to the chemisorption state is 1.5×10^{13} s^{-1} and the activation energy for the reaction is 0.283 eV.

Although the precursor-mediated chemisorption process has been theoretically[3,4,12] predicted in the adsorption of unsaturated hydrocarbons on Si(001), it seems that molecules in a precursor state have never been experimentally observed. For this reason, Nagao *et al.*[13] mentioned that their HREELS study for the adsorption of vinyl bromide on Si(001) was the first spectroscopic observation of a strongly bound precursor state. Note that vinyl bromide, where the Br atom with a relatively greater electronegativity replaces one H atom of ethylene, has a polar C═C bond, contrasting with a nonpolar C═C bond of ethylene. Nagao *et al.* believed that the precursor state becomes more stable because of the effect of the substituent Br, making possible its observation at the low temperature of 58 K.

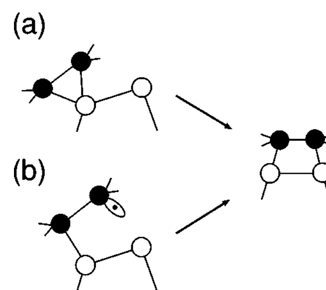

FIG. 1. Possible precursor states for the reaction of alkene on Si(001): (a) the three-atom intermediate model and (b) the diradical intermediate model.

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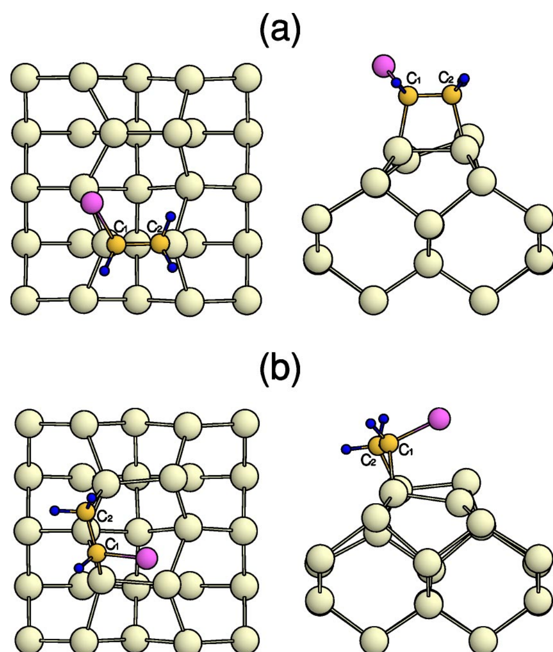

FIG. 2. Top and side views of the optimized structure of adsorbed vinyl bromide on Si(001): (a) the di-σ and (b) end-on chemisorption states. The circles represent Si, Br, C, and H with decreasing size.

In this paper, using first-principles density-functional theory calculations, we study not only the adsorption kinetics of vinyl bromide on Si(001) but also the dissociation of adsorbed vinyl bromide. We calculate the energy profile along the reaction pathways from the precursor state to the two kinds of chemisorption states, i.e., the di-σ [Fig. 2(a)] and end-bridge [Fig. 2(b)] states. The structure of our optimized quasiprecursor state belongs to a diradical intermediate model, rather than a three-atom intermediate model proposed by Nagao *et al.*[13] Our calculated energy profile for the reaction pathways shows that the chemisorption takes place without a barrier (hence quasiprecursor state), contrasting with the analysis of the HREELS (Ref. 13) data where the energy barrier from the precursor to the di-σ chemisorption state was estimated to be 0.283 eV. Interestingly, this energy barrier is very close to our calculated energy barrier ($\sim$0.30 eV) from the chemisorption state to the dissociative state. Based on our findings, the two chemisorption states, di-σ and end bridge, can be easily formed at 58 K without any activation energy, and will proceed to formation of the dissociative state with increasing temperature above $\sim$90 K. We will suggest a reinterpretation for the adsorption states observed[13] by the HREELS experiment.

The rest of the text is organized as follows. In Sec. II, the calculational method is described. In Sec. III, we determine the atomic structure of adsorbed vinyl bromide on Si(001) within the precursor, chemisorption, and dissociative states. We calculate the energy profile for the reaction pathways of vinyl bromide on Si(001) and compare the results with the interpretation of the recent HREELS data. Finally, a summary is given in Sec. IV.

TABLE I. Calculated adsorption energy of vinyl bromide on Si(001). P, T, C, and D indicate the precursor, transition, chemisorption, and dissociative states, respectively (see Figs. 3 and 4). T_{diss} indicates the transition state for C—Br dissociation.

Reaction path	State	E_{ads} (eV)
R_{I}	P [Fig. 3(a)]	0.24
	T [Fig. 3(b)]	0.26
	C [Fig. 2(a)]	1.87
	T_{diss} [Fig. 3(c)]	1.58
	D [Fig. 5(a)]	2.82
R_{II}	P [Fig. 4(a)]	0.26
	T [Fig. 4(b)]	0.29
	C [Fig. 2(b)]	1.79
	T_{diss} [Fig. 4(c)]	1.48
	D [Fig. 5(b)]	1.96

II. CALCULATIONAL METHOD

The total-energy and force calculations were performed by using first-principles density-functional theory[14] within the generalized-gradient approximation (GGA). We use the exchange-correlation functional of Perdew, Burke, and Ernzerhof[15] for the GGA. The norm-conserving pseudopotentials of Si, Br, and H atoms were constructed by the scheme of Troullier and Martins[16] in the separable form of Kleinman and Bylander.[17] For the C atoms whose $2s$ and $2p$ valence orbitals are strongly localized, we used the Vanderbilt ultrasoft pseudopotential.[18] The surface is modeled by a periodic slab geometry. Each slab contains six Si atomic layers and the bottom Si layer is passivated by two H atoms per Si atom. The thickness of the vacuum region between these slabs is about 13 Å, and vinyl bromide molecules are adsorbed on the unpassivated side of the slab. A plane-wave basis set was used with a 25 Ry cutoff, and the **k** space integrations were done with meshes of four **k** points in the 2×2 surface Brillouin zone. The bottom two Si layers were taken at their calculated bulk positions with a lattice constant of 5.475 Å. All other atoms were allowed to relax along the calculated Hellmann-Feynman forces until all the residual force components were less than 1 mRy/bohr.

III. RESULTS

We first optimize the atomic structure of adsorbed $CH_2{=}CHBr$ on Si(001) within two possible chemisorption states. One is the di-σ structure where vinyl bromide adsorbs on top of a single Si dimer. The other is the end-bridge structure where vinyl bromide adsorbs across the ends of two adjacent dimers. Each optimized structure, where one $CH_2{=}CHBr$ molecule is adsorbed within the 2×2 unit cell (i.e., 0.5 monolayer coverage), is shown in Figs. 2(a) and 2(b), respectively. The calculated adsorption energies (E_{ads}) and geometrical parameters (bond lengths and bond angles) for these structures are given in Tables I and II, respectively. We find that the di-σ structure has an adsorption energy of 1.87 eV, larger than that (E_{ads}=1.79 eV) of the end-bridge

TABLE II. Calculated bond lengths (d in Å) and bond angles (ϕ in degree) of vinyl bromide on Si(001) for the chemisorption and dissociative states.

State	$d_{C_1—C_2}$	$d_{C_1—Br}$	$d_{C_1—H}$	$d_{C_2—H}$	$d_{C_1—Si}$	$d_{C_2—Si}$	$d_{Br—Si}$	$\phi_{Si—C_1—C_2}$	$\phi_{Si—C_2—C_1}$	$\phi_{C_2—C_1—Br}$
C [Fig. 2(a)]	1.55	1.98	1.10	1.10	1.96	1.96		102.1	102.0	113.3
C [Fig. 2(b)]	1.55	2.01	1.10	1.11	1.99	1.97		116.2	114.8	110.5
D [Fig. 5(a)]	1.47		1.11	1.10	1.82	1.96	2.30	133.9	74.2	
D [Fig. 5(b)]	1.46		1.10	1.10	1.88	2.06	2.29	123.9	106.8	

structure. This tendency in the stability of the two chemisorption states is the same as the previous[19] results in C_2H_4/Si(001), where the di-σ (end-bridge) structure has E_{ads}=1.94(1.82) eV

For the [2+2] reaction of vinyl bromide on Si(001), the recent HREELS (Ref. 13) study proposed a strongly bound three-atom precursor [see Fig. 1(a)] where the two Si—C bond lengths are similar to each other. This precursor state is expected to be easily produced because of the energetically favored hybridization between the π bonding state of vinyl bromide and the empty dangling-bond state of the down atom of the buckled Si dimer. We tried to optimize the structure of the three-atom intermediate model, but it converged to the structure which has a single bond between the C_2 atom and the down Si atom [see Fig. 3(a)]. As shown in Fig. 3(a), the distance d_1=2.72 Å between the C_1 and the down Si atom is much longer than d_2=2.24 Å between the C_2 and the down Si atom. Thus, we can say that our optimized quasiprecursor state belongs to, rather than the three-atom intermediate model,[13] the diradical intermediate model. We refer to it as a quasiprecursor state rather than a precursor state because it is not a local energy minimum. We note that the double bond of CH_2=CHBr is partly polarized because of a

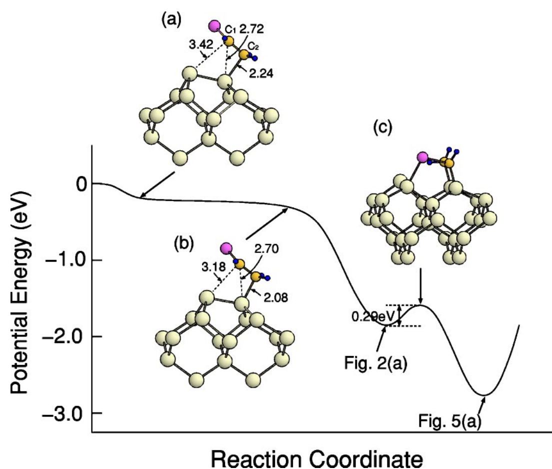

FIG. 3. Calculated energy profile for the reaction pathway I, forming the chemisorption state (i.e., di-σ structure) as well as its dissociative state. The atomic geometries of three representative points are given: (a) the precursor (P) state, (b) the transition (T) state, and (c) the transition (T_{diss}) state for formation of the dissociative state. The numbers denote the interatomic distances (in angstroms). The reaction coordinate from the precursor to the chemisorption state is $d_{C_1—Si}$, while that from the chemisorption to the dissociative state is $d_{Br—Si}$; see the text.

greater electronegativity of the Br atom compared to the C and H atoms. This charge asymmetry in CH_2=CHBr results in a C_2 atom more nucleophilic than the C_1. Consequently, the C_2 atom can be easily attracted to the down Si atom, as reflected by our results showing a shorter d_2 compared to d_1. As a matter of fact, the three-atom intermediate model was theoretically[19] proposed as a precursor in the adsorption of C_2H_4, which contains a nonpolar C=C bond. However, the three-atom precursor proposed by Nagao *et al.*[13] seems to be unlikely in the adsorption of CH_2=CHBr containing a polar C=C bond.

Next, we study the reaction pathways from the quasiprecursor state to the two chemisorption states. The reaction pathway forming the di-σ (end-bridge) structure is, hereafter, labeled as I (II). In order to find the minimum energy pathway, we optimize the structure by using the gradient projection method[20] where only the distance $d_{C_1—Si}$ (but not the angles) between the C_1 atom and its bonded (in the chemisorption state) Si atom is constrained. Therefore we obtain the energy profile for the reaction pathways as a function of decreasing distance $d_{C_1—Si}$. Here, Hellmann-Feynman forces aid in the relaxation of all the atomic positions as well as the C_1—Si bond angles for each fixed value of $d_{C_1—Si}$. The calculated energy profiles and the atomic geometries of the quasiprecursor and quasitransition states along the reaction pathways I and II are displayed in Figs. 3 and 4, respectively. Here quasitransition represents a state just before the rapid energy descent along the reaction pathway. If the quasiprecursor state were a true precursor state, then the quasitransition state would be at an energy maximum and would be a transition state. Since the quasiprecursor state and the quasitransition state are not minima and maxima, their exact positions on the reaction pathway are not uniquely defined. We note that the quasiprecursor state [Fig. 4(a)] where the C—C bond is in the (110) plane perpendicular to the Si dimer has an adsorption energy of 0.26 eV, similar to E_{ads} =0.24 eV of the quasiprecursor state [Fig. 3(a)] along the reaction pathway I. Along the two reaction pathways, we find a very flat energy profile between the quasiprecursor state and the quasitransition state and then a rapid increase of the adsorption energy beyond the quasitransition state, leading to formation of the chemisorption state. Here, the adsorption energy slopes monotonically between the quasiprecursor state and the quasitransition state (by less than 0.03 eV) so that there is no barrier along the reaction pathways. Since there is very little difference between the molecular bonding at the quasiprecursor and quasitransition points, it is possible that there is no barrier for the molecule to initially bond anywhere along the reaction pathway we have calculated be-

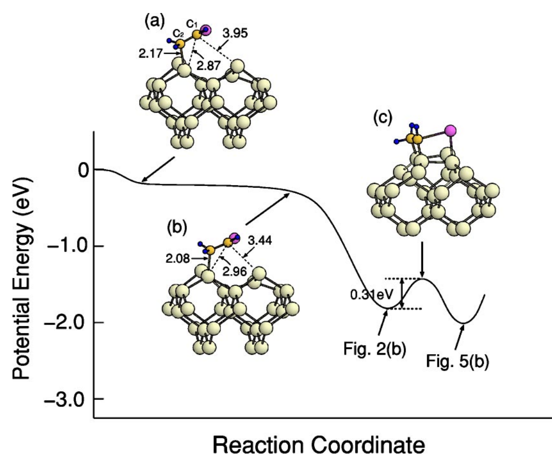

FIG. 4. Calculated energy profile for the reaction pathway II, forming the end-bridge structure as well as its dissociative state. The atomic geometries of three representative points are given: (a) the precursor (P) state, (b) the transition (T) state, and (c) the transition (T_{diss}) state for formation of the dissociative state. The numbers denote the interatomic distances (in angstroms). The reaction coordinate from the precursor to the chemisorption state is $d_{C_1—Si}$, while that from the chemisorption to the dissociative state is $d_{Br—Si}$; see the text.

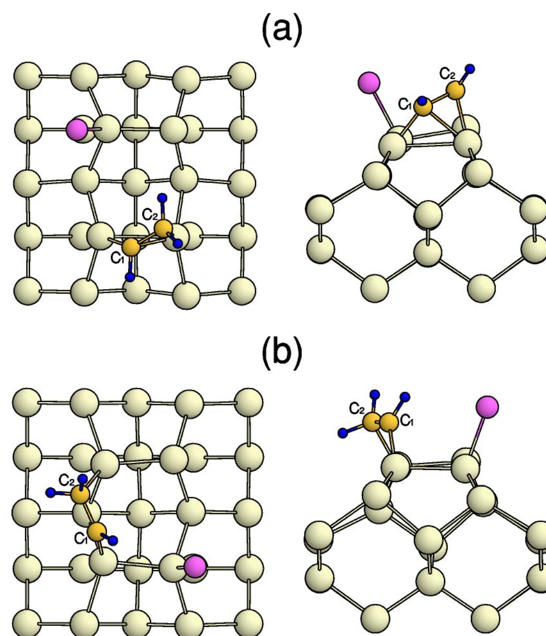

FIG. 5. Top and side views of the optimized structure of the dissociative state at the end of the reaction pathway (a) I and (b) II.

tween the quasiprecursor state and the quasitransition state.

Our calculated energy profiles along the reaction pathways are not consistent with the interpretation of the HREELS (Ref. 13) data, where vinyl bromide was trapped at the three-atom precursor state at 58 K. The existence of such a strongly bound precursor state has not been observed in the adsorption of any alkene on Si(001). Notably, our previous[19] calculations for C_2H_4 adsorption on Si(001) obtained an energy barrier of 0.02(0.12) eV from the three-atom precursor to the di-σ (end-bridge) chemisorption state. We believe that the diradical precursor of $CH_2{=}CHBr$ on Si(001) is likely to be more facile for the reaction as a consequence of the presence of a radical, as demonstrated by our calculated energy profiles.

From the HREELS (Ref. 13) spectra of vinyl bromide on Si(001), Nagao *et al.* observed that a vibration peak located at 439 cm^{-1} appears at 90 K and its intensity increases with increasing temperature. They attributed this peak to the Si—Br stretching mode, indicating that the C—Br bond cleavage takes place at 90 K. In order to understand this dissociation of adsorbed $CH_2{=}CHBr$, we calculate the energy profile for the C—Br bond cleavage. We optimize the atomic structure by using the gradient-projection method, where only the distance $d_{Br—Si}$ between the Br atom and its bonded (in the dissociative state) Si atom is constrained. The atomic geometries of the transition (T_{diss}) and dissociative (D) states along the reaction path I [II] are displayed in Figs. 3(c) and 5(a) [4(c) and 5(b)], respectively, and their adsorption energies are given in Table I. We find that the T_{diss} state along the reaction path I (II) has $E_{ads}=1.58(1.48)$ eV. Therefore, the di-σ (end-bridge) structure undergoes C—Br dissociation over an energy barrier of 0.29(0.31) eV (see Figs. 3 and 4). Using an Arrhenius-type activation process with a preexponential factor[13,21] of 1.5×10^{13} s^{-1}, we estimate that at 90 K the reaction rate from the di-σ (end-bridge) to the dissociative state is $\sim0.9\times10^{-3}(0.7\times10^{-4})$ s^{-1}. Thus, noting that exposure time in a previous[13] experiment was a few thousand seconds, thermal activation for the C—Br dissociation along the two reaction pathways is likely to occur at 90 K, consistent with the observation[13] of the Si—Br stretching mode.

From their HREELS spectra, Nagao *et al.*[13] observed that the intensity of the peak at 208 cm^{-1} decreases with increasing temperature from 58 K to 90 K, while a new peak at 1087 cm^{-1} appears at 90 K. Based on the precursor-mediated chemisorption mechanism, Nagao *et al.* interpreted the former and latter peaks as due to the precursor state and the di-σ chemisorption state, respectively. Using the Arrhenius analysis for the reaction from the precursor to the chemisorption state, Nagao *et al.* estimated its activation energy as 0.283 eV. We have to notice that this magnitude is very close to our calculated energy barrier of 0.29(0.31) eV from the di-σ (end-bridge) structure to the dissociative state of Fig. 5(a) [5(b)]. Since our calculated energy profiles for the reaction pathways do not support the existence of a strongly bound precursor state, we believe that the observed peaks at 208 cm^{-1} and 1087 cm^{-1} may originate from the chemisorption and dissociative states, respectively. Thus, the observed adsorption state at 58 K would be associated with the di-σ and end-bridge chemisorption states, whereas that above 90 K can be mostly associated with the dissociative states of Figs. 5(a) and 5(b).

IV. SUMMARY

We have performed first-principles density-functional calculations for the adsorption of vinyl bromide on Si(001). Our calculated energy profiles for the reaction pathways do not

support a recently proposed[13] adsorption picture which involves a strongly bound precursor state at a low temperature of 58 K. We found that vinyl bromide adsorbs on top of a single Si dimer or across the ends of two adjacent Si dimers without any activation energy and subsequently dissociates into the CH_2—CH and Br species over an energy barrier of ~0.30 eV. We are not able to identify the origin of the observed peaks (e.g., located at 208 cm^{-1} and 1087 cm^{-1}) from the HREELS (Ref. 13) experiment, but hope our proposed adsorption picture will stimulate a proper analysis of the HREELS data being done.

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