Reaction of 1,2-Dibromobenzene with the Si(111)-7×7 Surface, a DFT Study

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Reaction between 1,2-dibromobenzene and the Si(111)-7×7 surface has been studied theoretically on the DFT(B3LYP/6-31G(d)) level. A 12-atom silicon cluster, representing two adatoms and one rest atom of the faulted half of the unit cell, was used to model the silicon surface. The first step of the reaction was a covalent attachment (chemisorption) of an intact 1,2-dibromobenzene molecule to the silicon cluster. Binding energies were calculated to be between 1.04 and 1.14 eV, depending on the orientation of the molecule. A second step of the reaction was the transfer of the Br atom to the silicon cluster. Activation energies for the transfer of the Br atom were calculated to be between 0.4 and 0.6 eV, suggesting that the thermal bromination reaction occurs on a microsecond time scale at room temperature. A third step of the reaction could be the transfer of the second Br atom of the molecule, the desorption of the organic radical, or the change of the adsorption configuration of the radical, depending on the original orientation of the adsorbed intact molecule. A novel, aromatic, two-σ-bound adsorbed configuration of the C_6H_4 radical, in which a carbon ring of the radical is perpendicular to the silicon surface, has been introduced to explain previous experimental observations (*Surf. Sci.* **2004**, *561*, 11).

1. Introduction

Reactions between unsaturated organic molecules and the Si(111)-7×7 surface are actively studied now[1−26] because of their importance for building organosilicon nanodevices. Halo-substituted organomolecules R−X, where R stands for the organic radical, and X is a halogen atom, are of interest because the R−X chemical bond is relatively weak and molecules containing such bonds can efficiently react with silicon, both spontaneously and because of photon or electron impact[5−7,27,28]

Quantum chemistry calculations, which are necessary to understand the mechanisms of such reactions, are time consuming because of the large number of silicon atoms, which should be taken into account to represent a silicon surface properly. The challenge is to find a proper combination of the size of the silicon cluster and the appropriate level of theory. Clusters, which are too large, do not allow one to use a decent level of theory, while clusters, which are too small, may not represent the silicon surface properly.

Several theoretical studies of the adsorption and the reactions of aromatic compounds with the Si(111)-7×7 surface have been performed by using a large, 5-layer half-unit cell silicon cluster and semiempirical AM1 level of theory as well as a 3-layer silicon cluster and DFT(B3LYP/6-31G*) level of theory.[4] An activation energy for the transfer of the Cl atom from clorobenzene to the Si(111)-7×7 surface has been studied by using the DFT B3LYP/3-21G* approach and a 19-atom silicon cluster embedded into a large 5-layer 64-atom silicon cluster optimized by the Hartree−Fock theory.[16]

In other studies, relatively small silicon clusters were used in DFT calculations.[14,15] Fan and co-workers[15,29] showed that the DFT(B3LYP/6-31G(d,p)) level of theory can be successfully used for calculation of the adsorption of a chlorobenzene molecule on a 9-atom silicon cluster, which contains one adatom and one rest atom. The molecule adsorbs by opening a double bond of the carbon ring and forming a 1,4-cyclohexadiene type structure, which is attached to the silicon surface by two σ bonds.[22] This mechanism is similar to the mechanism of the adsorption of benzene.[30,31]

However, the 9-atom silicon cluster does not allow one to calculate a potential energy profile for the transfer of the halogen atom from the parent molecule to the silicon surface because both available silicon dangling bonds are already occupied by the adsorbed intact molecule. One more silicon adatom with a dangling bond should be taken into account to study the dynamics of the halogen atom transfer. To fulfill this condition, in the present work, a reaction between 1,2-dibromobenzene and the Si(111)-7×7 surface was studied by using a 12-atom silicon cluster on the DFT(B3LYP/6-31G(d)) level of theory.

The 12-atom silicon cluster (Figure 1) contains two silicon adatoms and one rest atom. The adsorbed intact molecule occupies one middle adatom, M(1), and the rest atom, while another silicon middle adatom, M(2), serves as an adsorption site for the Br atom that is being transferred from the parent molecule to the surface. The M(2) adatom was chosen because it is the closest one to the Br(2) atom of the intact molecule and is also close to the Br(1) atom. The theoretical results obtained in the present work are consistent with previous experimental findings,[10] which are briefly described below.

The experiment[10] shows that the reaction between dibromobenzene and the Si(111)-7×7 surface occurs spontaneously at room temperature and leads to the formation of adsorbed Br atoms and pairs of Br atoms partially accompanied by organic residues, such as C_6H_4Br and C_6H_4. The Br atoms, which comprise a pair, are most often adsorbed on silicon adatoms separated by 7.7 Å. A relative amount of Br pairs accompanied by organic residues has been found to decrease by approximately a factor of 5 if the deposition was done on a warm (45 °C) surface rather than at room temperature.

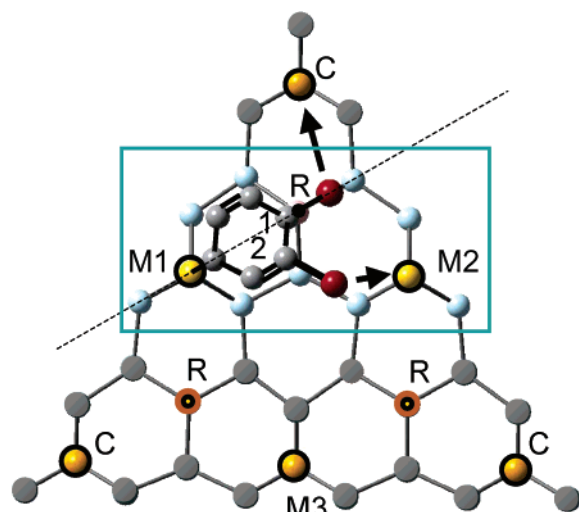* Corresponding author. E-mail: sdobrin@chem.utoronto.ca.

Figure 1. The 1,2-dibromobenzene molecule adsorbed on the middle adatom and the rest atom of the faulted half of the Si(111)-7×7 unit cell. Adatoms are circled and labeled "C" (corner) and "M" (middle). Rest atoms, "R", are marked by small circles. The carbon atom labeled "1" is attached to the silicon rest atom, and all other carbon atoms are numbered clockwise. A dashed line shows the C1−C4 axis of the molecule. Arrows show most plausible directions of the Br atom transfer to silicon. A fragment of the 7×7 unit cell, which was used in the DFT calculations, is highlighted.

For interpretation of the experimental results, two mechanisms of the reaction have been previously suggested:[10] a "Br-mediated" (termed later "daughter-mediated"[11]), and a "benzene-mediated" (termed also "parent-mediated"[11]). In the daughter-mediated case, the transfer of the Br atom from a dibromobenzene molecule to silicon occurs directly when the molecule approaches the silicon surface by its brominated part.[14] This mechanism was thought to produce adsorbed Br atoms and pairs of Br atoms, which are not accompanied by organic residues.

In the parent-mediated case, a 1,2-dibromobenzene molecule first attaches itself to two silicon atoms and forms an adsorbed 1,4-cyclohexadiene type structure. After the attachment, a transfer of the Br atom occurs from the parent molecule to silicon. Another Br atom can be transferred sequentially. The parent-mediated mechanism was thought to produce adsorbed intact molecules and organic residues accompanied by single Br atoms and pairs of Br atoms.

The results of the present DFT calculations suggest that the parent-mediated mechanism can fully describe the experimental observations,[10] and accounts for all types of the experimentally observed reaction products.

2. Model and Computational Details

A 1,2-dibromobenzene molecule adsorbed on the Si(111)-7×7 surface is shown in Figure 1. A 7×7 unit cell consists of two half-unit cells,[32,33] a faulted and an unfaulted one. Each half-unit cell contains nine silicon atoms that have dangling bonds. Among them, there are six adatoms, separated from each other by 7.7 Å, and three rest atoms, labeled **R**. Each rest atom is separated by 4.6 Å from the nearest adatom. The six adatoms, in turn, are subdivided into three middle adatoms **M 1**, **2**, and **3**, and three corner adatoms, **C**.

The dibromobenzene molecule, shown in Figure 1, is attached to the faulted half-unit cell of the silicon surface by two σ bonds, which connect two carbon atoms of the molecule with two silicon atoms, a middle adatom, and a rest atom. This adsorption configuration was chosen because the experiment[10] shows that the 1,2-dibromobenzene molecule prefers to adsorb on the

middle, rather than on the corner silicon adatom, and on the faulted half-unit cell rather than on the unfaulted one.

In DFT calculations, a 12-atom silicon cluster (Figure 2) was used. The cluster contains two silicon adatoms and one rest atom. Both a geometry optimization and a zero-energy vibrational energy (ZPE) correction were done on the B3LYP/6-31G(d) level of theory. During the geometry optimization only three silicon atoms, two adatoms and the rest atom, were allowed to move; the other nine silicon atoms were fixed in their positions. The calculations have been done by using the Gaussian-98 program package.[34]

To obtain an initial guess for the DFT calculations, a benzene molecule was first optimized on top of a large, 5-layer half-unit cell silicon cluster, which was prepared by using the data of Tong et al.[35] This optimization was done by using the AM1 level of theory[36] as has been described previously.[11] In the AM1 optimization, two middle adatoms and one rest atom were allowed to move, as well as nine silicon atoms from the underlying level, which are attached to the optimized adatoms and the rest atom. After the optimization, a 12-atom fragment of the large silicon cluster was selected and used in the DFT calculations of the adsorbed dibromobenzene molecule. Hydrogen atoms were used to terminate the dangling bonds of the bulk silicon atoms of the 12-atom cluster. The Si−H bond lengths were fixed at 1.5 Å. All initial guesses for the various configurations of the adsorbed 1,2-dibromobenzene molecule and radicals were prepared by replacing the corresponding H atoms of the benzene molecule with Br atoms (an initial guess for the C−Br bond length was 1.91 Å), or by removing H atoms to prepare required radicals.

The energy of adsorption of the intact molecule was calculated as the difference between the energy of the silicon cluster with attached molecule and a sum of the energy of the molecule in the gas phase and the energy of the bare silicon cluster. Such calculations were done for all adsorbed species (Table 1). The energetical balances of various reactions (Tables 2 and 3) were calculated as the differences in energies between reagents and reaction products.

The accuracy of the calculations was verified by comparison of the calculated desorption energy of benzene, 0.96 eV, with an experimental value of 0.95 eV[31,37] and with 0.97 eV, calculated for a 3-layer silicon cluster on the B3LYP/6-31G(d)[4] level. The value obtained in the present work is also in a good agreement with results of other theoretical works.[17,21,29]

It was verified that the binding energy of several adsorbed species could be calculated as a sum of the binding energies of the individual species. Such a test was performed for two adsorbed Br atoms. The desorption energy of a single adsorbed Br atom was calculated as 3.854 eV, while the desorption energy of the Br atom in the presence of another Br atom, adsorbed on another silicon adatom, was calculated to be higher by 14 meV. This energy difference is small. Hereafter, a mean value of 3.86 eV is used for the desorption energy of the Br atom.

In another test, the desorption energies of the C_6H_4Br radical alone and in the presence of an adsorbed Br atom were calculated. The obtained energies differed from each other by less than 10 meV, indicating that the lateral interaction between adsorbates is small.

Barriers for the Br transfer were calculated by using silicon clusters shown in Figure 2. In the calculation, a length of the C−Br bond was fixed at some intermediate value between 1.9 and 4.3 Å. All other parameters of the system were optimized, as has been done during the optimization of the equilibrium geometry of the adsorbed molecule. Two original guesses were
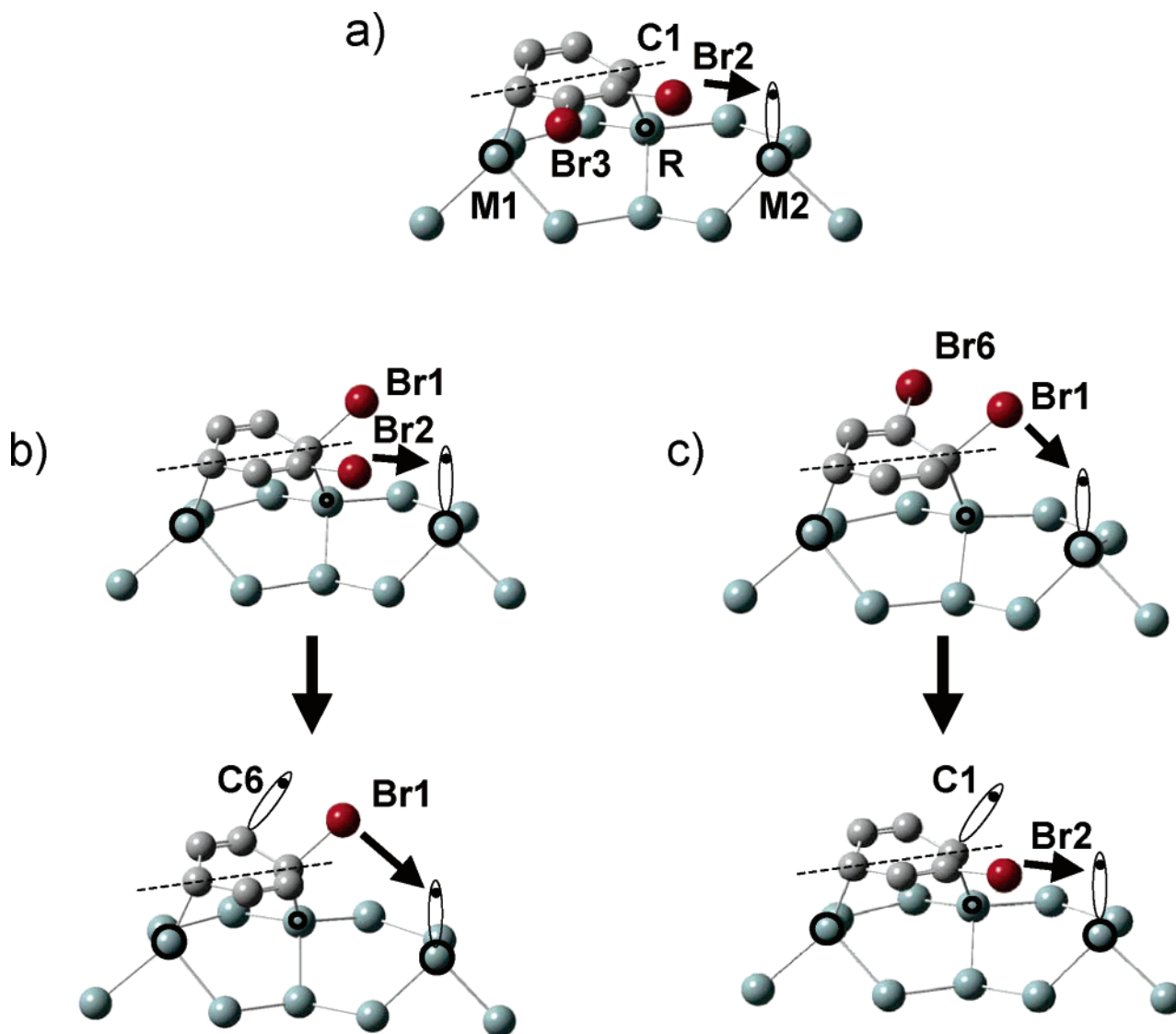
Figure 2. Various clusters used in the DFT calculations of the Br atom transfers. (a) Cluster used to model the transfer of the Br(2) atom from the intact molecule adsorbed in the 2,3- orientation. (b) Clusters used to model two sequential transfers of the Br atom, started by the transfer of the Br(2) atom of the intact molecule adsorbed in the 1,2- orientation. To calculate the transfer of the second Br atom, a dangling bond is placed on the C6 carbon atom, as if the Br atom from this position was already transferred to the corner silicon adatom. (c) Clusters used to model two sequential Br transfers started by the transfer of the Br(1) atom of the intact molecule adsorbed in the 1,2- orientation. The dashed line shows the C1–C4 axis of the molecule.

used in the optimization: (i) the C–Br bond was oriented in its original direction, as in the adsorbed intact molecule, and (ii) the C–Br bond pointed to the Si adatom. Between these two values of energy, the lower one has been chosen. An example of an energy profile is given in Figure 3. The barrier height calculated in such a way is an upper limit because of the restricted optimization.

To calculate the activation energy of the subsequent transfer of another Br atom, the silicon cluster containing a carbon atom with the dangling bond was used as if the Br atom from this position was already transferred to silicon. Multiplicity of the system was chosen to be $M = 3$ for the calculations of the adsorbed C_6H_4Br, and $M = 2$ for the adsorbed C_6H_4 radicals, because these configurations were found to be lower by energy.

3. Results and Discussion

3.1. Adsorption Energies of Intact Molecules in Various Orientations. The 1,2-dibromobenzene molecule can adsorb on the Si(111)-7×7 surface in six orientations. These orientations differ from each other by the positions of the Br atoms. In Figure

1, the carbon atom, which is attached to the rest silicon atom, is labeled 1, and all other carbon atoms are numbered clockwise. In the 1,2- orientation, shown in Figure 1, one Br atom is attached to the sp^3 hybridized C(1) atom, which is connected to the silicon rest atom by a σ bond; the second Br atom is attached to the carbon atom C(2), which is not σ-bound to the silicon surface. These two Br atoms will be termed Br(1) and Br(2) hereafter. In the 2,3- orientation, Br atoms are attached to the C(2) and C(3) carbon atoms; and in the 3,4- orientation, to the C(3) and C(4) carbon atoms.

The adsorption energies were calculated for 1,2-, 2,3-, and 3,4- orientations (Table 1) and were found to be close to each other, with the 1,2- orientation being the less stable configuration, with 1.03 eV desorption energy, and the 3,4- orientation being the most stable configuration, with 1.13 eV desorption energy. The difference between desorption energies in these two orientations is small in comparison with the total desorption energy. The calculated values are consistent with an experimental observation that intact molecules do not desorb from the silicon surface at temperature lower than 100 °C (ref 10).

TABLE 1: Adsorption Energies of Adsorbed Species, and Lengths of C−Si σ Bonds[a]

	desorption energy (eV)		literature			
adsorbed particle	ZPE corrected	no ZPE	data (eV)	symbol	C−Si(R) Å	C−Si(M) Å
1,2- intact molecule	1.03	1.14	n.a.	E_{M12}	2.00	2.00
2,3- intact molecule	1.05	1.17	1.99[b]	E_{M23}	2.04	1.99
3,4- intact molecule	1.13	1.24	0.91[1]	E_{M34}	2.02	1.98
1,2−R₁ (1*, Br(2))	2.25	2.37		$E_{R1(1)}$	1.92	2.08
1,2−R₁ (6*, Br(1))	1.26	1.38		$E_{R1(6)}$	1.99	2.00
1.2−R₁ (Br(1), 2*)	1.29	1.41		$E_{R1(2)}$	1.99	2.01
2,3−R₁ (2*, Br(3))	1.24	1.38	1.27[b]	$E_{R1(23,2)}$	2.00	2.00
1,2−R₂ (6*, 1*)	2.22	2.37		E_{R2}	1.91	2.01
R₁ (1σ)	2.55	2.68		$E_{R1σ}$	1.92	
R₂ (1σ)	3.02	3.13		$E_{R2σ}$	1.89	
R₂ (2σ v)	4.34	4.51	5.3[c]	$E_{R2σV}$	1.95	1.94
Br(ads)	3.86	3.95	3.9[d]; 4.2[d]	E_{Br}		2.23
C−Br bond dissociation energy in isolated molecule						
for the first Br atom	3.55	3.64	3.5 eV[3]	E_{BDE1}		
for the second Br atom	2.59	2.65		E_{BDE2}		

[a] R₁ = C₆H₄Br; R₂ = C₆H₄; asterisk indicates the dangling bond on the carbon atom. R₁(1σ) stands for the one-σ-bound "vertical" C₆H₄Br(v) radical; R₂(1σ) for the one-σ-bound vertical C₆H₄(v) radical, and R₂(2σ v) for the two-σ-bound vertical C₆H₄(v 2σ) radical. [b] Ref 11. [c] Ref 39. [d] BDE (Si−Br), ref 41.

TABLE 2: Reactions from the 2,3- Orientation of the Adsorbed 1,2-Dibromobenzene Molecule

	energy eV				activation barrier for	literature
	ZPE corrected	no ZPE	literature data	calculations	the Br atom transfer eV	data
molecule in the gas phase	0.0					
adsorbed molecule	1.05	1.17	1.99[a]	E_{M23}		
R₁(2*Br(3)) + Br(ads)	1.55	1.69	1.61[a]	$E_{R1(23,2)} + E_{Br} − E_{BDE1}$	0.47	0.70[a]
R₁(gas) + Br(ads)	0.31	0.30	0.45[a]	$E_{Br} − E_{BDE1}$		

[a] Ref 11.

TABLE 3: Energies of Products and Intermediates Formed in Reactions Started from the 1,2- Orientation of the Adsorbed 1,2-Dibromobenzene Molecule

	energy (eV)			activation barrier
species	ZPE corrected	no ZPE	calculation	for the Br atom transfer (eV)
molecule in the gas phase	0.0	0.0		
adsorbed molecule	1.03	1.14		
Sequential Transfers of Br Atoms Which Begins by the Transfer of the Br(2) Atom (Figure 5).				
R₁(Br(1),6*) + Br(ads)	1.57	1.69	$E_{R1(6)} + E_{Br} − E_{BDE1}$	0.51 M₁,₂ → R₁(Br(1),2*) + Br
R₂ (1*,2*) + 2Br(ads)	3.81	3.98	$E_{R2} + 2E_{Br} − E_{BDE1} − E_{BDE2}$	0.48 R₁(Br(1),6*) → R₂(1*,6*) + 2Br
Sequential Transfers of Br Atoms Which Begins by the Transfer of the Br(1) Atom (Figure 7).				
R₁(1*, Br(2)) + Br(ads)	2.56	2.68	$E_{R1(1)} + E_{Br} − E_{BDE1}$	0.47 M₁,₆ → R₁(1*,Br(6)) + Br
R₂ (1*, 2*) + 2Br(ads)	3.81	3.98	$E_{R2} + 2E_{Br} − E_{BDE1} − E_{BDE2}$	0.59 R₁(1*,Br(2)) → R₂(1*,2*) + 2Br
Energies of Reaction Products				
R₁(gas) + Br(ads)	0.31	0.31	$E_{Br} − E_{BDE1}$	
R₂(gas) + 2Br(ads)	1.59	1.61	$2E_{Br} − E_{BDE1} − E_{BDE2}$	
R₁(1σ) + Br(ads)	2.85	2.99	$E_{R1σ} + E_{Br} − E_{BDE1}$	
R₂(1σ) + 2Br(ads)	4.65	4.74	$E_{R2σ} + 2E_{Br} − E_{BDE1} − E_{BDE2}$	
R₂(2σ Vert) + 2Br(ads)	5.93	6.12	$E_{R2σV} + 2E_{Br} − E_{BDE1} − E_{BDE2}$	

The most striking difference between the present results and the previous AM1 calculations[11] is the difference between the binding energy of an intact molecule adsorbed in the 2,3-orientation, 1.99 eV according to AM1, and 1.05 eV according to the DFT calculations (Table 1). According to the AM1 results, the 2,3- and 5,6- orientations are the most stable ones. Activation energies for the transfers of the Br(2) and Br(3) atoms from the parent molecule to the silicon middle adatoms M(2) and M(3) were calculated by AM1 to be 0.70 and 1.69 eV, respectively, with respect to the intact molecule. The higher activation energy for the latter transfer is not surprising because the Br(3)−M(3) distance is much longer than the Br(2)−M(2) one. It was realized[11] that the new Br−Si bond is forming while the old C−Br bond is breaking so that the activation energy decreases. A large, ∼1 eV, difference between the activation energies of the Br(3) atom transfer to the M(3)

and M(2) silicon adatoms indicates that the Br−Si separation is important for the probability of the thermal transfer of the Br atom.

Present DFT results show that all orientations of the intact molecule are plausible. This finding, together with the fact that the Br−Si distance strongly affects the rate of the Br transfer, suggests that the transfer of the Br atom is most likely to occur from the positions 1- and 2- of the parent molecule to the corner and M(2) silicon adatoms. The Br(1)−Si(corner) separation is approximately 4.0 Å, and the Br(2)−Si(M(2)) separation is 3.1 Å. The Br atoms attached to the C(3) and C(4) carbon atoms are much further from the adjacent silicon adatoms with separation distances longer than 5 Å. The transfer of the Br(5) atom can occur to the silicon corner adatom or to the adatom of another unit cell. However both silicon adatoms are far from the Br(5) atom. The transfer of the Br(6) atom to the corner
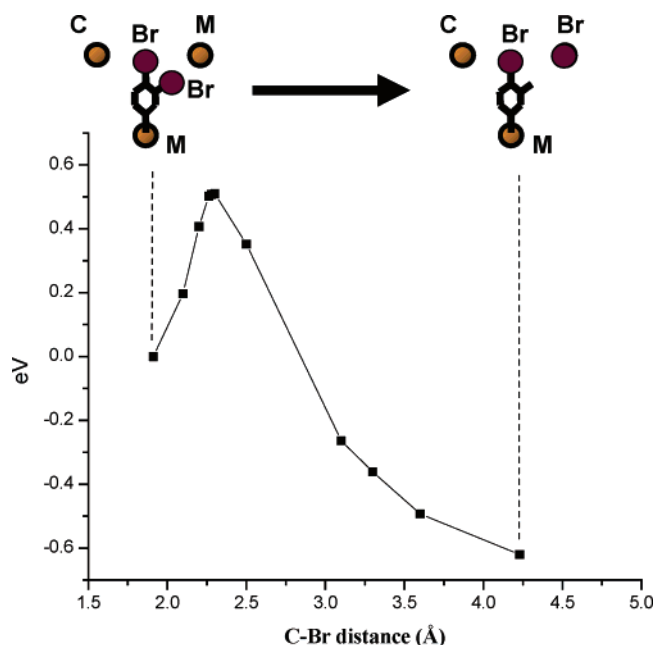
Figure 3. Potential energy profile for the transfer of a Br atom from position 2, of the intact molecule adsorbed in the 1,2- orientation. The leftmost and the rightmost points of the plot correspond to the equilibrium structures, with the Br atom attached to the parent molecule and to the silicon adatom, respectively.

Figure 4. Energy diagram for the reaction triggered by the transfer of the Br(2) atom from the intact molecule adsorbed in the 2,3- orientation. The solid line shows the Br transfer and the dashed line shows desorption of the radical. Framed schematics show stable products of the reaction.

adatom is plausible and is assumed to be similar to the transfer of the Br(2) atom to the M(2) silicon adatom.

As a conclusion, reactions which lead to the fast transfer of the single Br atom and to the formation of pairs of Br atoms separated by 7.7 Å can be understood by considering the sequential transfer of the Br atom from 1- and 2- positions of molecules and radicals adsorbed in the 1,2- orientation and the transfer of the single Br atom from the position 2 of the parent molecule adsorbed in the 2,3- orientation. These processes are discussed in the following sections.

3.2. Reaction Initiated by the Transfer of the Br(2) Atom from the 2,3- Orientation of the Intact Molecule. A 1,2-dibromobenzene molecule adsorbed in the 2,3- orientation can undergo the transfer of the Br(2) atom to the silicon surface (Figure 2a). An energy diagram of the reaction is shown in Figure 4. The transfer of the Br(2) atom to the adjacent silicon adatom requires $E = 0.47$ eV of activation energy (Table 2). It follows, therefore, that at room temperature, a thermal transfer of the Br(2) atom will occur during ~ 10 μs (calculated using a usual form, $\tau = A \exp(E/k_BT)$ with a preexponential factor of $A = 10^{-13}$ s). This reaction can be written as

$$C_6H_4Br_2(ads) + Si \rightarrow C_6H_4Br(3)(ads) + SiBr$$
$$\Delta E = -0.5 \text{ eV}$$
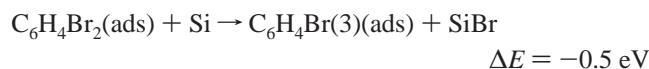
where Si stands for the unoccupied silicon adatom. After the transfer of the Br(2) atom, an adsorbed $C_6H_4Br(ads)$ organic residue and an adsorbed nearby Br atom are formed. The reaction is exothermic by 0.5 eV.

Alternatively, instead of residing on the surface, the newly formed C_6H_4Br residue can desorb to the gas phase. The desorption energy of the $C_6H_4Br(3)(ads)$ radical was found to be 1.24 eV (Table 1). At room temperature, thermal desorption with such an activation energy is a very slow process. However, desorption of the radical can be assisted by the energy released in the two preceding steps of the reaction, which are the adsorption of the intact molecule and the transfer of the Br(2)
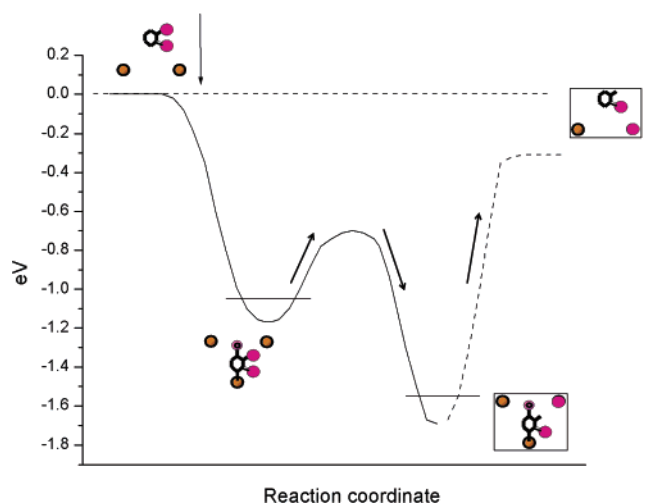
atom. The whole process, which includes the adsorption of intact molecule, the transfer of the Br atom, and desorption of the radical is exothermic by 0.3 eV (Table 2), and therefore is energetically possible. In the experiment, only the stable products of the reaction, i.e., adsorbed Br atoms partially accompanied by organic residues, can be observed.[10]

An activation energy for the transfer of the Br(3) atom was estimated to be higher than 1.5 eV. This high activation barrier makes the thermal transfer of the Br(3) atom practically impossible at room temperature.

As a conclusion, the reactions initiated by the thermal transfer of the Br(2) atom from the 2,3- orientation of the intact molecule mainly produce adsorbed Br atoms partially accompanied by 1,4-cyclohexadiene-type C_6H_4Br organic residues.

3.3. Reaction Initiated by the Transfer of the Br(2) Atom from the 1,2- Orientation of the Intact Molecule. A molecule adsorbed in the 1,2- orientation can undergo the thermal transfer of either Br(1) or Br(2) atoms. In this section, reactions triggered by the transfer of the Br(2) atom of the intact molecule are considered (Figure 2b). An energy profile for the transfer of the Br(2) atom along the C(2)−Br(2)−Si(M(2)) reaction coordinate is shown in Figure 3, and an energy diagram of the whole reaction is shown in Figure 5. The transfer of the Br(2) atom requires an activation energy of 0.51 eV and is exothermic by 0.57 eV (Table 3). The transfer does not affect the binding of the organic residue to the surface strongly. The binding energy increases by only 0.26 eV, and the C(1)−Si(R) bond becomes shorter by 0.01 Å (Table 1). The reaction can be written as

$$C_6H_4Br_2(ads) + Si \rightarrow C_6H_4Br(1)(ads) + SiBr$$
$$\Delta E = -0.57 \text{ eV} \quad (1)$$
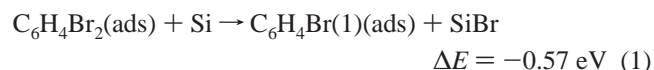
After the transfer of the Br(2) atom to the silicon M(2) middle adatom, the subsequent transfer of the Br(1) atom to the silicon corner adatom can occur. To find a potential barrier of the reaction, the transfer of the Br(1) atom to the corner silicon adatom was modeled by the Br(1) atom transfer to the M(2) middle adatom because the corner adatom is not included in the silicon cluster that was used in the calculations (Figure 2b). This is a reasonable approximation because of the symmetry of the system (Figure 1). The transfer was found to require 0.48 eV of activation energy. The small activation energy indicates
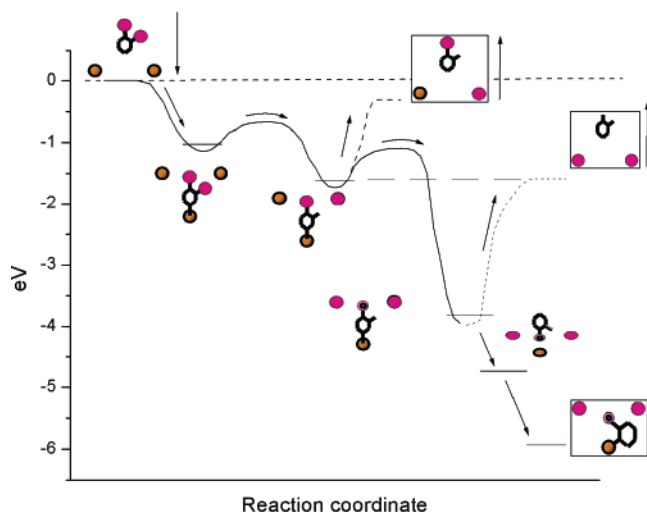
Figure 5. Energy diagram for the reaction triggered by the transfer of the Br(2) atom from the intact molecule adsorbed in 1,2- orientation. The solid line shows the Br transfer, the dashed curves show desorption of the radical, and arrows show the change of the geometry of adsorbed radicals. Framed schematics show stable products of the reaction.

that the transfer of the Br(1) atom occurs quickly at room temperature, similarly to the transfer of the Br(2) atom.

$$C_6H_4Br(1)(ads) + Si \rightarrow C_6H_4(ads) + SiBr$$
$$\Delta E = -2.24 \text{ eV} \quad (2)$$
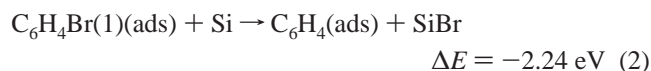
The transfer of the Br(1) atom affects the binding of the organic residue much more strongly than the preceding transfer of the Br(2) atom. Binding energy increases by ~1 eV, and the C(1)−Si(rest) bond length becomes shorter by 0.08 Å (Table 1). This strong increase in the binding energy can be accounted for by the change of the hybridization of the C(1) atom in the $sp^3 \rightarrow sp^2$ direction. The net bromination reaction is the result of the steps (1) and (2), and can be written as,

$$C_6H_4Br_2(ads) + 2Si \rightarrow C_6H_4(ads) + 2SiBr$$
$$\Delta E = -2.81 \text{ eV}$$
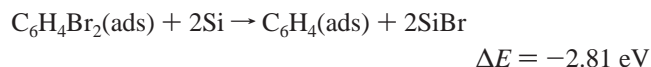
This equation does not describe the whole reaction, however, because the $C_6H_4(ads)$ structure, formed after the transfer of both Br atoms, is unstable at room temperature. This adsorption state can be converted into the one-σ-bound structure, $C_6H_4(v)$, with the radical staying "vertically" on the Si(rest) atom (Figure 6). The one-σ-bound state is lower by 0.8 eV than the two-σ-bound structure (R$_2$(1σ) vs 1,2-R$_2$(6*,1*), Table 1). The one-σ-bound state was suggested previously, for interpretation of the photoinduced H atom transfer from benzene to the Si(111)-7×7 surface,[16] and was studied theoretically in several works[4,15,29] This transformation of the radical can be described as

$$C_6H_4(ads) \rightarrow C_6H_4(v) \qquad \Delta E = -0.80 \text{ eV} \quad (3)$$

The newly formed $C_6H_4(v)$ radical is highly vibrationally excited, with excessive energy concentrated in the pendulum-like motion of the whole radical on top of the silicon rest atom and in the C(1)−Si(rest) stretch mode. The C(1)−Si(rest) bond became vibrationally excited because the equilibrium length of the C(1)−Si(rest) bond changes from 1.91 Å in $C_6H_4(ads)$ configuration to 1.89 Å in the $C_6H_4(v)$ structure, Table 1. The energy released in the transfer of the Br(1) atom from the parent $C_6H_4Br(ads)$ radical is enough to

trigger the desorption of the daughter C_6H_4 radical, as can be seen from Table 3 and the energy diagram (Figure 5).

$$C_6H_4Br(1)(ads) + Si \rightarrow C_6H_4(v) + SiBr \rightarrow$$
$$C_6H_4(gas) + SiBr \qquad \Delta E = -0.01 \text{ eV} \quad (4)$$
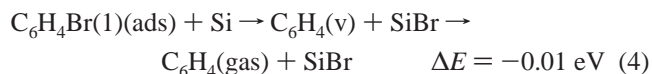
One should bear in mind that the newly formed $C_6H_4(v) +$ SiBr system has an additional 0.48 eV of kinetic energy, which the system gained by "falling down" from the potential barrier. Desorption of the radical leads to the formation of a pair of two Br atoms adsorbed on adjacent silicon adatoms, separated by 7.7 Å. Such pairs of Br atoms were commonly observed in the experiment.[10]

Another possible consequence of the formation of the $C_6H_4(v)$ vertical radical is the transformation of the radical into a two-σ-bound adsorbed structure, $C_6H_4(v\ 2\sigma)$, with the carbon ring perpendicular to the silicon surface (Figure 6).

$$C_6H_4(v) \rightarrow C_6H_4(v\ 2\sigma) \qquad \Delta E = -1.32 \text{ eV} \quad (5)$$

The formation of such an adsorbed structure is plausible because the $C_6H_4(v)$ radical has a dangling bond located on the C(2) carbon atom, to which the Br(2) atom was attached before.[38] The $C_6H_4(v\ 2\sigma)$ radical is bound to the surface more strongly than the one-σ-bound $C_6H_4(v)$ residue by 1.32 eV, and by 2.12 eV stronger than the cyclohexadiene-type $C_6H_4(ads)$ radical (Table 1). The $C_6H_4(v\ 2\sigma)$ structure resembles the C_6H_4 residue adsorbed on the Si(100)-2×1 surface, where the C_6H_4 radical links two Si atoms in two adjacent dimer rows.[39,40]
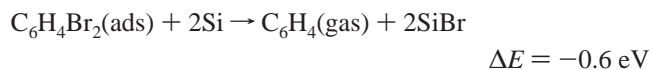
The $C_6H_4(v\ 2\sigma)$ adsorbed residue preserves its aromaticity, contrary to the 1,4-cyclohexadiene type $C_6H_4(ads)$. The out-of plane C_6H_4 organic residue can be considered as benzyne (C_6H_4) attached to the silicon surface by opening a triple carbon−carbon bond of the molecule.

In the experiment,[10] both the isolated Br pairs, and the Br pairs accompanied by the organic residues, have been observed. It has been found that the small (from 25 to 45 °C) increase in the surface temperature causes a large, approximately by a factor of 5, decrease in the relative number of organic residues accompanying the Br pairs. This observation is in accord with the present study, in which the rate of desorption of radicals is determined by the surface temperature and by the rate of dissipation of the excessive vibrational energy. At elevated temperatures, the probability of desorption is higher, and the newly formed $C_6H_4(v)$ radicals may not have enough time to rotate along the C(1)−Si(rest) bond and to form the $C_6H_4(v\ 2\sigma)$ structure. As a result, a larger fraction of the radicals can desorb from the surface.

The net reactions triggered by the thermal transfer of the Br(2) atom from the intact molecule adsorbed in the 1,2- orientation can be written as:

$$C_6H_4Br_2(ads) + 2Si \rightarrow C_6H_4(v\ 2\sigma) + 2SiBr$$
$$\Delta E = -4.9 \text{ eV}$$
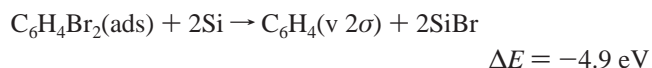
Or, in the case of desorption of the radical:

$$C_6H_4Br_2(ads) + 2Si \rightarrow C_6H_4(gas) + 2SiBr$$
$$\Delta E = -0.6 \text{ eV}$$

As can be seen from these equations, the reactions initiated by the thermal transfer of the Br(2) atom from the 1,2- orientation of the intact molecule, mainly produce adsorbed Br pairs partially accompanied by vertical $C_6H_4(v\ 2\sigma)$ organic residues.
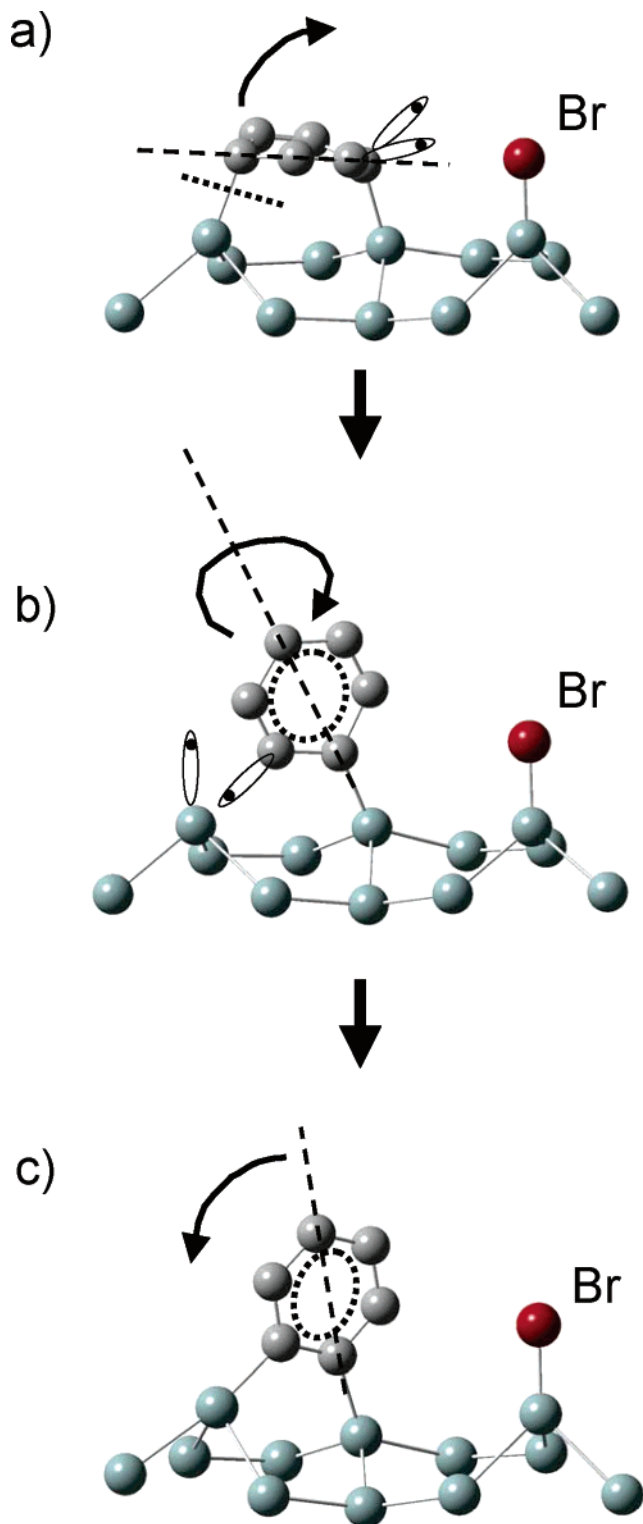
a)

b)

c)

Figure 6. The transformation of the 2-σ-bound state of the in-plane C₆H₄ radical to the one-σ-bound, and then to the two-σ-bound out-of-plane states. First step is the scission of the C—Si(middle) σ bond, which is followed by the formation of a plane carbon ring which is one-σ bound to the silicon rest atom. The dashed line shows the C(1)—C(4) molecular axis. After rotation of the carbon ring around the C—Si bond, a second σ bond is formed between the Si adatom and the carbon atom number 2.

3.4. Reaction Initiated by the Transfer of the Br(1) Atom from the 1,2- Orientation of the Intact Molecule. In this case, the Br(1) atom attached to the C(1) carbon atom is transferred to the silicon surface first (Figure 2c). It can go to either corner
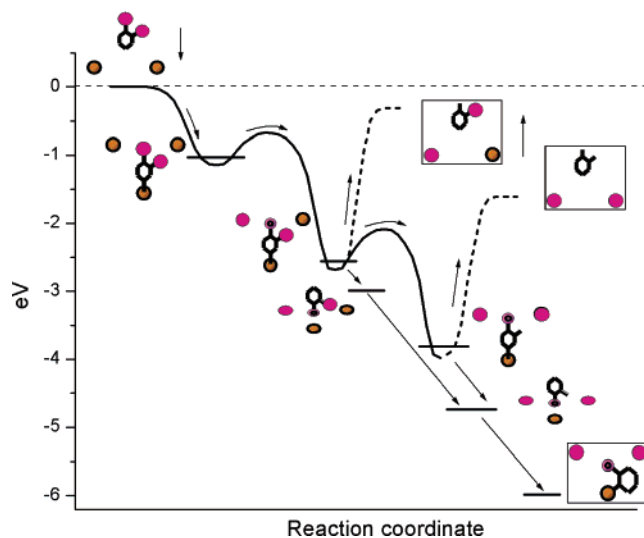

Figure 7. Energy diagram for the reaction triggered by the transfer of the Br(1) atom from the parent molecule adsorbed in the 1,2- orientation. The solid line shows the Br transfer, the dashed curves show the desorption of the radical, and arrows show the change of the geometry of adsorbed radicals. Framed schematics show stable products of the reaction.

or middle silicon adatoms. An energy diagram of this reaction is shown in Figure 7. To get to the nearest silicon middle adatom, M(2), the Br(1) atom should overcome a barrier of 0.47 eV (Table 3). This potential barrier was used in Figure 7 to represent the barrier for the transfer of the Br(1) atom to the nearest corner silicon adatom. It was necessary because the corner silicon adatom was not included in the silicon cluster used in the calculations. The transfer of the Br(1) atom increases the binding energy of the radical by 1.2 eV and shortens the length of the C—Si(rest) bond by 0.08 Å (Table 1). The physical reason for this increase in the binding energy is the change of the hybridization of the C(1) atom in the sp³ → sp² direction, similar to the transfer of the Br(1) atom from the C₆H₄Br radical considered in the previous section.
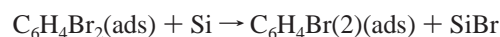
$$C_6H_4Br_2(ads) + Si \rightarrow C_6H_4Br(2)(ads) + SiBr$$
$$\Delta E = -1.53 \text{ eV}$$

The transfer of the Br(1) atom to the corner adatom can be followed by two further processes: (i) the transfer of another atom of the molecule (i.e., the Br(2) atom) to the middle adatom, or (ii) by the transformation of the adsorbed C₆H₄Br(ads) radical from the two-σ-bound state to the vertical one-σ-bonded state, C₆H₄Br(v) (Figure 8). Formation of the vertical one-σ-bonded state, C₆H₄Br(v), is also possible after the transfer of the Br(1) atom to the middle adatom These reaction pathways are discussed below.

(i) The subsequent transfer of the Br(2) atom requires 0.59 eV activation energy and is exothermic by 1.25 eV. It can be described as,
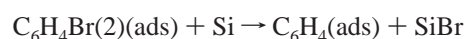
$$C_6H_4Br(2)(ads) + Si \rightarrow C_6H_4(ads) + SiBr$$
$$\Delta E = -1.25 \text{ eV}$$

The transfer of the Br(2) atom can be followed by the transformation of the 1,4-cyclohexadiene-type C₆H₄(ads) structure to the one-σ-bound vertical state C₆H₄(v), and then to the two-σ-bound C₆H₄(v 2σ) vertical structure, as described by eqs 3 and 5 in Section 3.3. Alternatively, the C₆H₄(v) vertical radical can desorb because of the cleavage of the C(1)—Si(rest) σ bond.
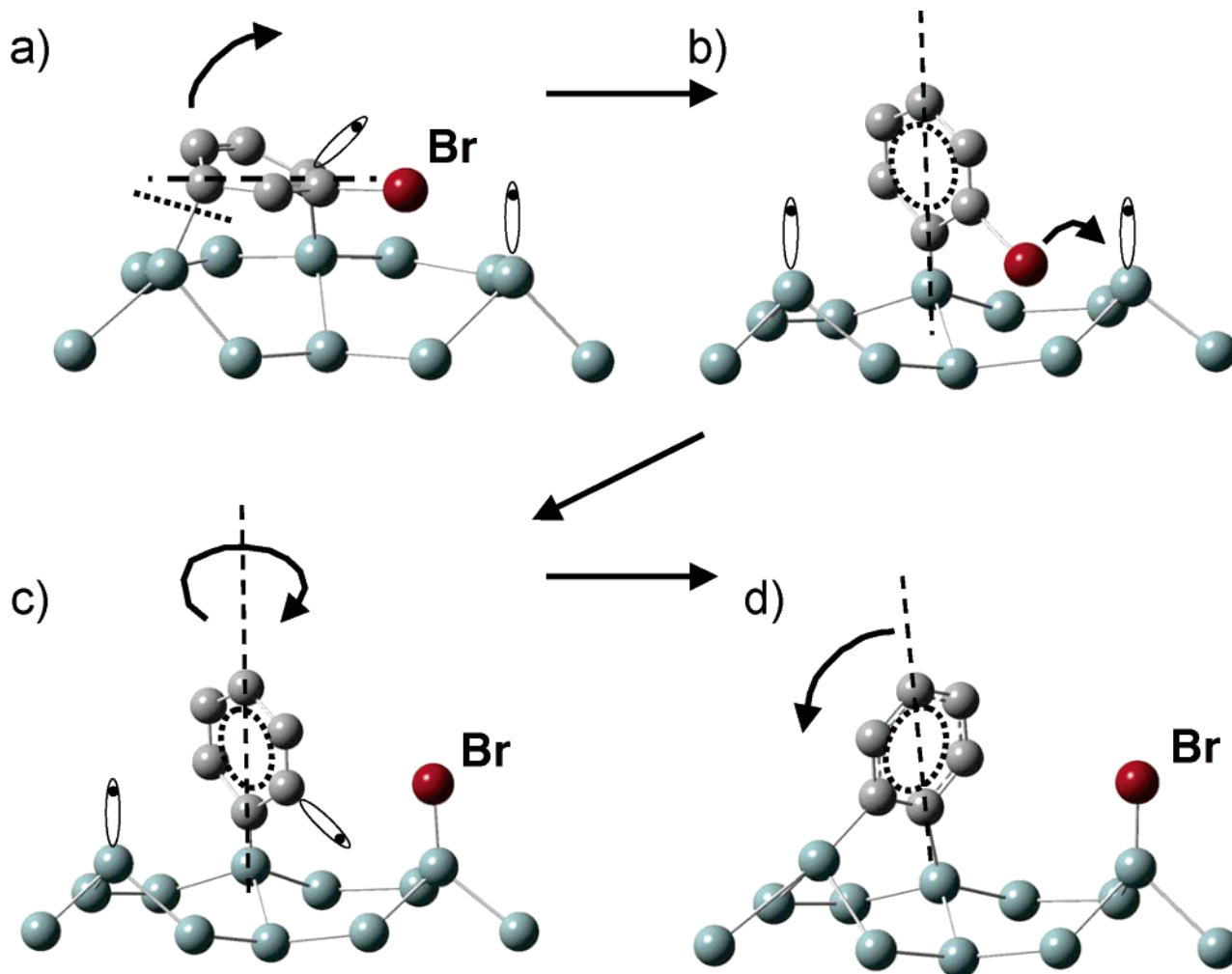
Figure 8. The transformation of the two-σ-bound state of the in-plane C$_6$H$_4$Br radical to the one-σ-bound, and then to the two-σ-bound out-of-plane states. First step is the scission of the C−Si(middle) σ bond, which is followed by the formation of a plane carbon ring which is one-σ bound to the silicon rest atom (b). The dashed line shows the C(1)−C(4) molecular axis. A Br atom transfer to the silicon adatom is a second step (b). Third step of the transformation is the rotation of the carbon ring around the C−Si bond (c), and formation of the second σ bond between the Si adatom and the carbon atom number 2 (d).

(ii) Another process, which can occur after the transfer of the Br(1) atom, and which competes with the transfer of the Br(2) atom (i), is the change of the adsorption geometry of the C$_6$H$_4$Br organic residue. The transformation from the 1,4-cyclohexadiene-type C$_6$H$_4$Br(ads) state to the vertical C$_6$H$_4$Br(v) state (Figure 8) is plausible because it is exothermic by 0.3 eV.

$$C_6H_4Br(2)(ads) \rightarrow C_6H_4Br(v) \qquad \Delta E = -0.3 \text{ eV}$$

As has been discussed above (Section 3.3), the newly formed organic residue is highly vibrationally excited, so that the C(1)−Si(rest) bond can break. In this case, the C$_6$H$_4$Br radical desorbs, leaving on the surface an isolated Br atom.

$$C_6H_4Br_2(ads) + Si \rightarrow C_6H_4Br(v) + SiBr \rightarrow$$
$$C_6H_4Br(gas) + SiBr \qquad \Delta E = +0.72 \text{ eV}$$
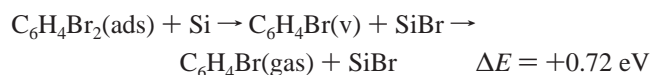
This process is endothermic and is only possible if assisted thermally or by the energy release due to the adsorption of the intact molecule, 1.03 eV. The endothermicity of the reaction makes it less plausible than the desorption of the C$_6$H$_4$(v) radical after the transfer of the Br(1) atom described in Section 3.3.

As another possibility, instead of the desorption, the newly formed vertical C$_6$H$_4$Br residue can undergo the transfer of the Br(2) atom to the silicon surface.

$$C_6H_4Br(v) + Si \rightarrow C_6H_4(v) + SiBr$$
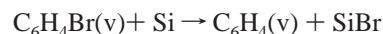
After the transfer of the Br(2) atom to the silicon surface, the C$_6$H$_4$(v) residue can desorb

$$C_6H_4(v) \rightarrow C_6H_4(gas)$$
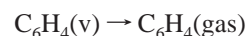
or turn around the C(1)−Si(rest) bond to form the C$_6$H$_4$ two-σ-bound out-of-plane aromatic structure, which is energetically favorable, as was discussed in Section 3.3.

$$C_6H_4(v) \rightarrow C_6H_4(v\ 2\sigma)$$
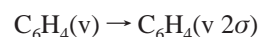
In this case, a pair of adsorbed Br atoms accompanied by organic residue is formed on the surface. The net reaction can be written as:

$$C_6H_4Br_2(ads) + 2Si \rightarrow C_6H_4(v\ 2\sigma) + 2SiBr$$
$$\Delta E = -4.9 \text{ eV}$$
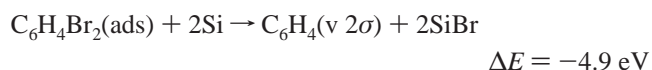
In summary, the reactions triggered by the thermal transfer of Br(1) atom from the intact molecule adsorbed in the 1,2-orientation most likely lead to the formation of adsorbed pairs of Br atoms partially accompanied by adjacent vertical C_6H_4(v 2σ) organic residues.

4. Conclusions

Reactions between 1,2-dibromobenzene and the Si(111)-7×7 surface have been studied theoretically on the DFT (B3LYP/6-31G(d)) level of theory by using a small 12-atom silicon cluster that represents two middle adatoms and one rest atom of the faulted half of a unit cell. Results of the present calculations are consistent with the previous experimental findings[10] and suggest that the reaction occurs spontaneously at room temperature through a covalent attachment of the intact 1,2-dibromobenzene to the silicon surface. The adsorption of the intact molecule occurs in a benzene-like way by forming a 1,4-cyclohexadiene type of the adsorbed structure. Binding energies were calculated to be between 1.04 and 1.14 eV, depending upon the orientation of the molecule.

The activation energies for the Br atom transfer were calculated to be between 0.4 and 0.6 eV, suggesting that the thermal bromination reaction at room temperature occurs on a microsecond time scale.

Yield of the reaction depends on the initial orientation of the adsorbed intact molecule. The reactions from the 1,2- and 1,6-orientations mainly produce adsorbed Br pairs partially accompanied by aromatic C_6H_4 organic residues, as well as single Br atoms, which are not accompanied by the C_6H_4Br organic residues. The reaction from the 2,3- and 5,6- orientations mainly produces single Br atoms partially accompanied by cyclohexadiene-type C_6H_4Br organic residues. The Br transfer from the molecules adsorbed in the 3,4- and 4,5- orientations is much less probable.

Desorption of the organic radical from the surface is most likely to occur through the metastable one-σ-bound state, in which the radical makes a pendulum-like motion on top of the silicon rest atom. As a result of such a motion, the C(1)−Si(rest) bond becomes stretched and can be broken. In this case, one adsorbed Br atom or a pair of two adsorbed Br atoms will remain on the surface.

A novel, two-σ-bound out-of plane adsorbed configuration of the C_6H_4 radical (Figure 8) has been introduced to explain the previous experimental observations.[10] In this configuration, the carbon ring of the radical is perpendicular to the silicon surface. The radical in this adsorption state preserves its aromaticity. Keeping aromaticity is important in attaching organic molecules to silicon in potential nano-electronic applications. The C_6H_4 radical adsorbed in the two-σ-bound out-of-plane state can serve as a linking element between the silicon surface and the long-chain organic molecule containing a variety of functional groups, which can be used in building molecular nanodevices.

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