The Mechanism of 1,2-Addition of Disilene and Silene: Hydrogen Halide Addition**

Balázs Hajgató,[a] Masae Takahashi,[b] Mitsuo Kira,[c] and Tamás Veszprémi*[a]

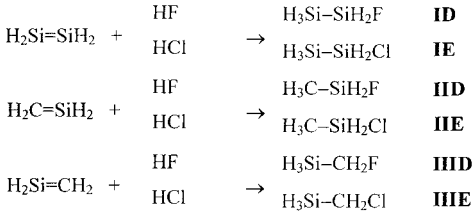
Abstract: The mechanism of 1,2-addition reactions of HF and HCl to Si=Si, Si=C, and C=C bonds has been investigated by ab initio quantum chemical methods. Geometries and relative energies of the stationary points and all the transition states were determined by using the MP2/6-311++G(d,p), B3LYP/6-311++G(d,p), and CBS-Q levels of theory. The investigated reactions can be characterized by two main thermodynamic profiles. The type in which the reagent molecule attacks a carbon atom is moderately exothermic with a high activation barrier. The second type in which a hydrogen halide attacks a silicon is strongly exothermic with a low activation energy. At the early stage of all the reactions a weakly bonded initial complex is found which indicates that the initial step of all the reactions is an electrophilic attack of hydrogen halide. The geometry and charge distribution of the transition state of the reactions indicate two main types of mechanism. If silicon is attacked, the halogen–silicon bond formation precedes the H–Y bond breaking. If, however, carbon is attacked, the first step is always an ionic dissociation of the hydrogen halide and a carbenium ion formation, which is stabilized by the C–Y bond formation in the final step of the reaction. The reaction diagrams and proposed mechanisms explain the experimentally found regioselectivity well.

Keywords: ab initio calculations · disilene · reaction mechanisms · silicon

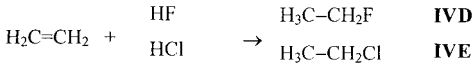
Introduction

In our previous papers[1] we reported the results of high level ab initio calculations for the mechanism of water and alcohol addition to disilene (designated by **IA–C**), silene (**IIA–B**, **IIIA–B**), and, as a comparison, ethene (**IVA–B**). The investigated reactions could be characterized by two main thermodynamic profiles. The type in which the reagent molecule attacks a carbon atom is moderately exothermic with a high activation barrier. If, however, water or alcohol attacks a silicon, the reaction is strongly exothermic, and the activation energy is small. Weakly bonded and characteristic complexes have been found at the early stage of all the reactions which determine the further mechanism. On the basis of the HOMO, LUMO, and Laplacian of electron distribution of disilene and silene two main mechanisms, an "electrophilic" and a "nucleophilic" channel, have been proposed depending on the substrate (disilene, silene, or ethene) and the reagent (water, methanol, or trifluoromethanol). The mechanisms assumed explain the experimentally found regioselectivity and diastereoselectivity well.

In this paper we report the systematic results of high level ab initio calculations for the mechanism of the following reactions.



For comparison we also studied the HF and HCl addition to ethene.



Unsaturated silicon species react efficiently with alcohol, water, and hydrogen halides without an acid catalyst to give

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addition products.[2] The addition to silenes results normally in a reaction forming silylethers, silanols, or halosilanes, and the "abnormal" way to give carbon-substituted silanes has never been observed.[3]

The first observations about the reactivity of disilenes suggested that the hydrogen halide addition reactions resembled those of electron-rich olefins.[4] The detailed investigations discovered differences. The reaction of stereoisomeric disilene (*E*)-1,2-di-*tert*-butyl-1,2-dimesityldisilene with HCl and alcohols is reported to give a mixture of two diastereomers.[5] From this result it was suggested that these reactions proceed in a stepwise manner involving a rate-determining nucleophilic (or electrophilic) attack in the first step. The zwitterionic intermediate formed in this step reacts further either by an intramolecular or intermolecular mechanism forming *syn* or *anti* product, respectively. Nagase and Kudo in their early theoretical calculations for the gas-phase HCl addition to disilene and silene found that the reaction involved a four-membered transition state and proceeded in a concerted manner.[6] According to Hartree–Fock calculations the barrier of the reactions was much smaller than in the similar reaction of ethene.

It is generally accepted that the hydrogen halide addition to olefins in the solution phase proceeds ionically, through a protonation as a first step, and the reaction yields a carbenium ion intermediate. The direct bimolecular addition which is the reverse of the HY elimination from haloalkanes, occurs in the gas phase by pyrolysis. This reaction has been studied extensively in recent years.[7] The leading interaction in the addition reaction with ethene was found to be an electrophilic attachment of the hydrogen atom of hydrogen halide to the carbon in ethene. The reactants form first a T-shaped van der Waals complex of C_{2v} symmetry, then with a rotation of HY within the heavy atom plane the reaction leads to a four-membered ring transition state and finally to the addition product. The conclusive evidence was gathered by both theory[8] and experiments[9] concerning the existence of the initial van der Waals complex.

It was also found that the termolecular reactions of ethene with two HF or HCl molecules are favored over the bimolecular channels owing to a catalytic action of a second hydrogen halide molecule.[7a–c] Although this might also be true in the reactions of silene or disilene, we discuss only the bimolecular reaction between the double bonded species and one hydrogen halide. The reactions with a dimer will be considered in future work.

Computational Methods

Quantum chemical calculations were carried out by using the Gaussian 94 and Gaussian 98 suite of programs.[10] In our previous work on the addition mechanism of 4-silatriafulvene[1a] we studied the effect of basis sets and electron correlation by using the standard 6-31G(d), 6-311++G(d,p), and 6-311++G(3df,2p) basis sets and several correlation methods like MP2, MP3, MP4SDQ, and QCISD. We found that the geometry was not sensitive to the basis set. However, considerable difference between the Hartree–Fock and correlated methods was observed. In our preceeding study on the mechanism of water and alcohol addition to doubly bonded systems[1d] excellent results could be gained by the CBS-Q method[11] for the thermodynamic data, and by the MP2 and B3LYP methods[12, 13] with the 6-311++G(d,p) basis set for the molecular geometry. Therefore in the present work we used the same levels of theory. Transition states for the reactions were fully optimized by using the eigenvector following method. Each reaction path was confirmed by intrinsic reaction coordinate (IRC) calculations by using the MP2/6-311++G(d,p) level. Second derivatives and harmonic vibrational frequencies were also calculated for all the stable molecules and transition states investigated. The existence of only one imaginary frequency for the transition states was checked. All the calculated energy data were corrected by the zero point energy (ZPE). For all the adduct molecules, a BSSE (Basis Set Superposition Error) correction was carried out according to the counterpoise procedure.[14]

For electron densities, a Natural Bond Orbital analysis was applied.[15]

Results and Discussion

The calculated thermodynamic data and selected geometric parameters are shown in Tables 1 and 2, respectively. Since the MP2 and B3LYP methods give very similar molecular geometry, only the MP2 results are presented in Table 2. Complete geometries and total energies for each stationary

Table 1. Thermodynamic data of stationary points in reactions **I**–**IVE**, and E in kcal mol^{-1}.

Reaction	Stat. point	CBS-Q		MP2[a]		B3LYP[a]	
		ΔE	ΔG^{298}	ΔE	ΔG^{298}	ΔE	ΔG^{298}
$H_2Si{=}SiH_2 + HF$ (**ID**)	reagents	0.0	0.0	0.0	0.0	0.0	0.0
	C_E	−2.2	2.9	−0.9	5.2	−2.4	3.8
	T	4.0	12.6	6.2	14.5	3.6	11.9
	P_f	−72.1	−63.9	−68.8	−60.9	−66.7	−58.8
$H_2Si{=}SiH_2 + HCl$ (**IE**)	reagents	0.0	0.0	0.0	0.0	0.0	0.0
	C_E	−2.7	1.7	−0.3	5.6	−0.3	5.7
	T	8.5	17.0	12.0	20.3	9.0	17.3
	P_f	−66.4	−57.9	−64.5	−56.3	−60.6	−52.4
$H_2C{=}SiH_2 + HF$ (**IID**)	reagents	0.0	0.0	0.0	0.0	0.0	0.0
	C_E	−3.6	2.6	−3.2	3.3	−4.5	2.4
	T	3.1	11.6	4.3	13.0	2.3	10.8
	P_f	−80.7	−72.4	−74.5	−65.9	−84.1	−65.7
$H_2C{=}SiH_2 + HCl$ (**IIE**)	reagents	0.0	0.0	0.0	0.0	0.0	0.0
	C_E	−3.3	2.9	−1.7	4.8	−2.4	4.5
	T	7.0	15.0	8.3	17.0	5.7	13.9
	P_f	−72.7	−64.1	−68.7	−59.9	−66.4	−57.8
$H_2Si{=}CH_2 + HF$ (**IIID**)	reagents	0.0	0.0	0.0	0.0	0.0	0.0
	C_E	−3.6	2.6	−3.2	3.3	−4.5	2.4
	T	49.3	57.8	53.9	62.6	42.4	50.9
	P_f	−21.3	−13.0	−18.4	−9.9	−21.9	−13.6
$H_2Si{=}CH_2 + HCl$ (**IIIE**)	reagents	0.0	0.0	0.0	0.0	0.0	0.0
	C_E	−3.3	2.9	−1.7	4.8	−2.4	4.5
	T	44.3	52.4	52.3	61.0	38.0	46.4
	P_f	−31.2	−22.6	−30.8	−22.0	−28.2	−19.6
$H_2C{=}CH_2 + HF$ (**IVD**)	reagents	0.0	0.0	0.0	0.0	0.0	0.0
	C_E	−3.3	2.0	−1.7	3.9	−2.6	3.1
	T	48.5	56.1	50.6	58.2	42.9	50.4
	P_f	−11.4	−3.9	−9.3	−1.6	−11.3	−3.7
$H_2C{=}CH_2 + HCl$ (**IVE**)	reagents	0.0	0.0	0.0	0.0	0.0	0.0
	C_E	−2.4	2.6	−0.7	4.8	−1.1	4.4
	T	41.7	49.1	46.0	53.7	37.1	44.7
	P_f	−16.8	−8.9	−17.6	−9.7	−13.9	−6.1

[a] Using 6-311++G(d,p) basis. C_E energies and free energies were corrected with the CP method.

Table 2. Selected geometric data[a, b] of reactions **I**–**IVD** and **E**.

Reaction	Stat. point	Geometric data[c]						Charge[d]			
$H_2X^1{=}X^2H_2 + HY$		$r(X^1X^2)$	$r(YH)$	$r(X^2Y)$	$r(XH)$	α_2	α_1	X^2	X^1	H	Y
	reagents	2.162	0.916			145.1	−145.1	0.304	0.304	0.539	−0.539
$H_2Si{=}SiH_2 + HF$ (**ID**)	C_E	2.162	0.925		2.743	−148.3	148.1	0.325	0.262	0.538	−0.562
	T	2.267	0.988	2.107	2.194	175.2	113.5	0.768	−0.046	0.507	−0.574
	P_f	2.342		1.632		124.4	120.1	1.125	0.431		−0.633
	reagents	2.162	1.273			145.1	−145.1	0.304	0.304	0.238	−0.238
$H_2Si{=}SiH_2 + HCl$ (**IE**)	C_E	2.164	1.282		2.933	−145.8	146.3	0.325	0.278	0.238	−0.262
	T	2.276	1.349	2.614	2.266	176.0	106.9	0.701	−0.033	0.240	−0.237
	P_f	2.337		2.069		124.1	119.7	0.702	0.489		−0.363
	reagents	1.710	0.916			180.0	180.0	0.980	−1.036	0.539	−0.539
$H_2C{=}SiH_2 + HF$ (**IID**)	C_E	1.714	0.930		2.097	174.3	169.6	1.050	−1.131	0.550	−0.574
	T	1.740	1.036	2.145	1.702	176.1	153.9	1.270	−1.282	0.508	−0.584
	P_f	1.856		1.629		124.9	121.6	1.548	−1.096		−0.634
	reagents	1.710	1.273			180.0	180.0	0.980	−1.036	0.238	−0.238
$H_2C{=}SiH_2 + HCl$ (**IIE**)	C_E	1.713	1.287		2.267	174.4	170.1	1.031	−1.101	0.254	−0.276
	T	1.732	1.482	2.817	1.581	178.2	158.4	1.265	−1.224	0.234	−0.418
	P_f	1.859		2.064		124.2	121.1	1.168	−1.068		−0.374
	reagents	1.710	0.916			180.0	180.0	−1.036	0.980	0.539	−0.539
$H_2Si{=}CH_2 + HF$ (**IIID**)	C_E	1.714	0.930		2.097	169.6	174.3	−1.131	1.050	0.550	−0.574
	T	1.850	1.126	1.811	1.855	167.1	121.1	−0.421	0.502	0.326	−0.484
	P_f	1.898		1.406		123.7	119.3	−0.304	0.930		−0.391
	reagents	1.710	1.273			180.0	180.0	−1.036	0.980	0.238	−0.238
$H_2Si{=}CH_2 + HCl$ (**IIIE**)	C_E	1.713	1.287		2.267	170.1	174.4	−1.101	1.031	0.254	−0.276
	T	1.811	1.632	2.460	1.746	176.6	131.4	−0.555	0.664	0.086	−0.326
	P_f	1.889		1.789		122.3	118.6	−0.805	0.980		−0.038
	reagents	1.338	0.916			180.0	180.0	−0.345	−0.345	0.539	−0.539
$H_2C{=}CH_2 + HF$ (**IVD**)	C_E	1.341	0.924		2.297	179.3	179.3	−0.364	−0.364	0.548	−0.561
	T	1.404	1.290	1.884	1.321	166.4	154.5	0.015	−0.700	0.431	−0.572
	P_f	1.510		1.397		124.0	120.5	0.116	−0.590		−0.396
	reagents	1.338	1.273			180.0	180.0	−0.345	−0.345	0.238	−0.238
$H_2C{=}CH_2 + HCl$ (**IVE**)	C_E	1.340	1.280		2.521	179.3	179.3	−0.357	−0.357	0.249	−0.260
	T	1.397	1.783	2.459	1.275	173.1	158.6	−0.042	−0.671	0.358	−0.529
	P_f	1.514		1.786		123.4	120.4	−0.336	−0.576		−0.060

[a] Calculated at the MP2/6-311 ++ G(d,p) level. [b] Bond lengths in Å, bond angles in degrees. [c] α_1 and α_2 are the dihedral angles between the HX^1H plane and X^1–X^2 bond and the HX^2H plane and X^2–X^1 bond, respectively. [d] NBO charges.

point are collected in the Supporting Information. Compared with the MP2, DFT, and CBS-Q methods, the MP2-computed thermodynamic data are generally closer to the highly accurate CBS-Q than the DFT results.

Similarly to the water and alcohol addition, the mechanism of the investigated reactions can be characterized by two different thermodynamic profiles (Table 1, Figures 1–6). When a halogen is bonded to a carbon atom (reactions **III** and **IV**), the reaction is moderately exothermic ($\Delta E > -32$ kcal mol^{-1}) with high (>40 kcal mol^{-1}) activation energy. On the other hand, when a halogen is bonded to a silicon atom (reactions **I** and **II**), the barrier is small (<9 kcal mol^{-1}), and the reaction is strongly exothermic ($\Delta E < -66$ kcal mol^{-1}). These findings are consistent with the experimental results: the addition to silicon always occurs in a facile bimolecular way, and hydrogen halide additions to silenes result normally in halosilanes. The gas-phase addition to olefins, however, requires high activation energy, and in the solution phase the reaction proceeds ionically with an acid catalyst.

Initial complexes: The initial step of all the addition reactions is the formation of a weakly bonded van der Waals complex. In water and alcohol addition, two main reaction profiles have been found.[1b, d] The path which starts with an "electrophilic" complex, C_E, clearly demonstrates an electrophilic interaction between one of the water/alcohol–hydrogens and the HOMO of disilene, and the reaction finishes with a *syn* product. In a second channel, the initial step is the formation of a "nucleophilic" complex, C_N, in which the lone electron pair of the oxygen turns toward the LUMO lobe of disilene. This reaction type is responsible for the *anti*-oriented products.

In the case of the hydrogen halide additions regardless of the substrate molecule, only a C_E-type initial complex has been found, in which the hydrogen of HY (where Y = F, Cl) points almost perpendicularly to the plane of the substrate, and this suggests the electrophilic attack on both carbon and silicon (Figures 1–6). Considering the strongly acidic character of the HY hydrogen, the lack of the nucleophilic channels is understandable. In the case of ethene + HY the adducts have a clear C_{2v} symmetry (T-shape). The disilene complexes are of similar shape with a slight asymmetry (C_s symmetry) due to the *trans*-bent structure of disilene. In the case of silene, the hydrogen points toward the negative carbon atom with a C_s symmetry. In contrast to the water and alcohol addition of silene, only one initial complex has been found, and, as IRC

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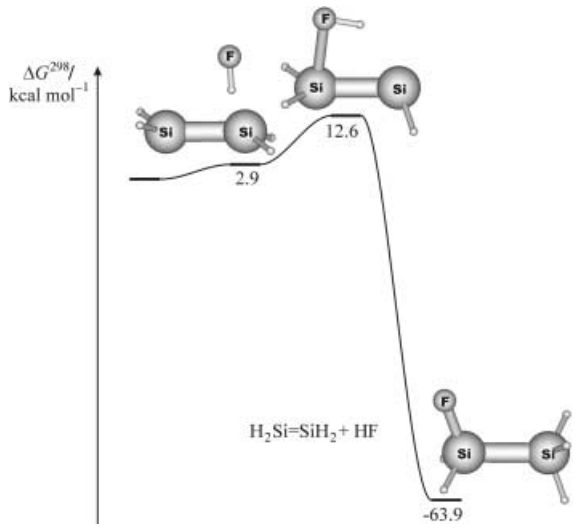

Figure 1. Free-energy diagram at the CBS-Q level of theory for the reaction channels of the disilene + hydrogen fluoride reaction (**ID**).[18]

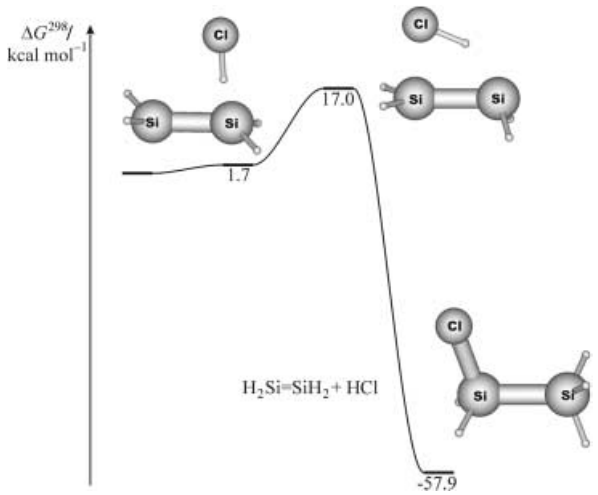

Figure 2. Free-energy diagram at the CBS-Q level of theory for the reaction channels of the disilene + hydrogen chloride reaction (**IE**).

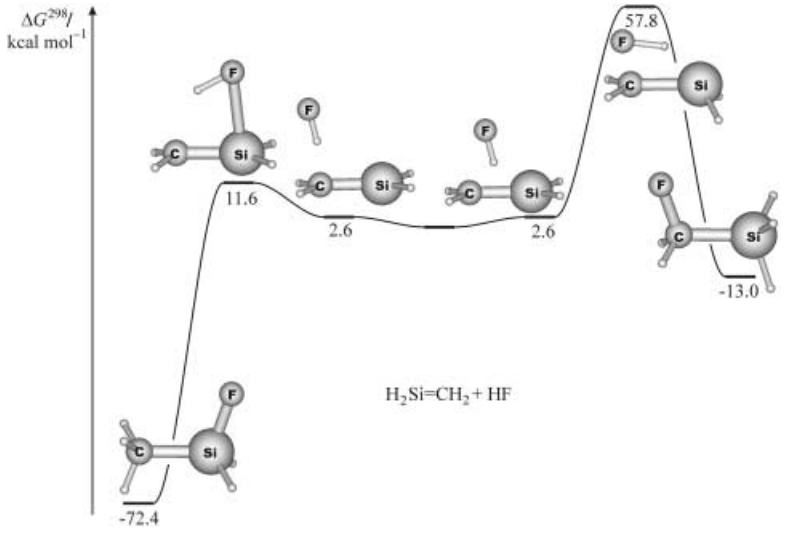

Figure 5. Free-energy diagram at the CBS-Q level of theory for the reaction channels of the silene + hydrogen fluoride reaction (**IID** and **IIID**).

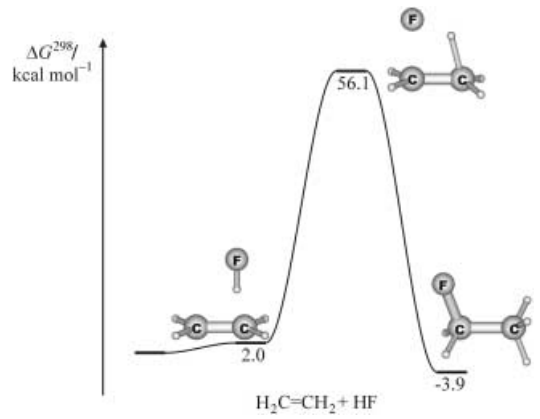

Figure 3. Free-energy diagram at the CBS-Q level of theory for the reaction channels of the ethene + hydrogen fluoride reaction (**IVD**).

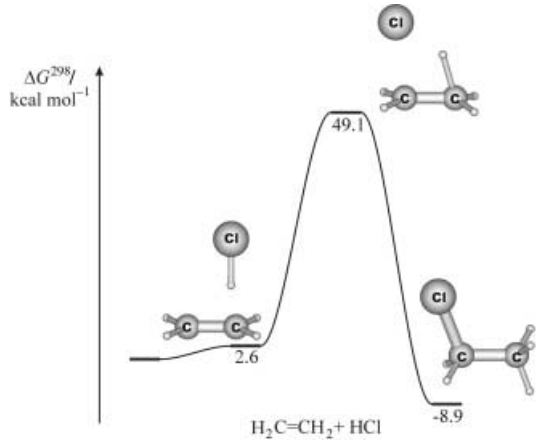

Figure 4. Free-energy diagram at the CBS-Q level of theory for the reaction channels of the ethene + hydrogen chloride reaction (**IVE**).

calculations prove (Figure 7), the reaction channels in both directions (**IID** – **IIID** and **IIE** – **IIIE**) start from the same C_E complex.

The stabilization energy of the complexes is between 2.2 and 3.6 kcal mol^{-1}, and the Gibbs free energy is a small positive value (between 1.7 and 2.9 kcal mol^{-1}) due to the negative entropy factors. The distance between the substrate molecule and the approaching hydrogen is between 2 and 3 Å, and for HCl it is larger than for HF by about 0.2 Å. The length of the double bond is practically unchanged, but the hydrogen – halogen bond is slightly elongated by about 0.007 – 0.014 Å in the complex. A small but systematic charge transfer from the substrate to the HY molecule (Table 2) proves the electrophilic character of the processes. It is an interesting fact that the negative charge on the HY moiety of the complex seems to be almost independent of the substrate and the type of halogen, and in each case it is found in a narrow region

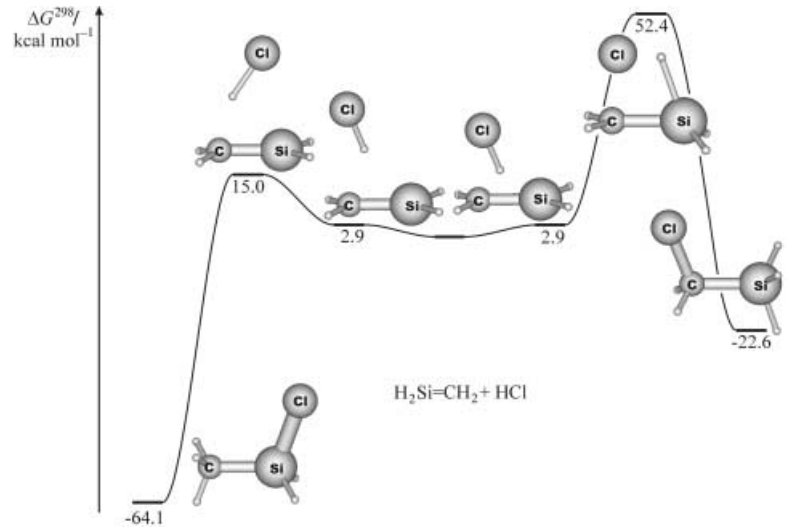

Figure 6. Free-energy diagram at the CBS-Q level of theory for the reaction channels of the silene + hydrogen chloride reaction (**IIE** and **IIIE**).

between −0.012 e and −0.024 e. Excluding the olefins, the charge shift region is even narrower (between −0.022 e and −0.024 e). The shape of the orbitals in the complexes is usually very similar to that of the separated component molecules. The shift of the orbital energies, however, indicates a trend, which is understandable on the basis of the FMO (Frontier Molecular Orbital) theory. The electrophilic interaction between the LUMO of the reagent and the HOMO of the substrate results in a slight shift of HOMO down and LUMO up.

Transition states: Starting from the initial van der Waals complex, a characteristic step of the water or alcohol addition is the formation of a Lewis complex via a transition state with low energy.[1] Then, in the next step it gives the final product (P_f) via a second transition state. The appearance of this second stable complex, however, depends on the type of alcohol. For example, in the case of the acidic CF_3OH, no second complex was found, and the reaction proceeded by the C_E-T-P_f channel. As a consequence, a similar reaction path is expected in the reactions with the strongly acidic hydrogen halides.

Although the structure of the transition states (T) is close to the geometry of the second transition state of the water and alcohol reactions,[1c, d] and it indicates the well-known four-membered ring character, some important differences can be observed between the reactions of disilene, silene, and ethene with hydrogen halides. In the case of **ID** and **IE** the Si atom closer to the halogen becomes almost planar, while the other silicon (closer to hydrogen) is pyramidal. The Si–Si bond is elongated, and it is more than halfway between the single and double bond. The Si–Y bond is shorter than the Si–H(Y) bond (compared with the final bond lengths), and the H–Y bond is only moderately elongated (by 6–8%). The π bond of disilene has already been broken, and the HOMO is localized on the pyramidal silicon as a formal lone electron pair. As a result, this silicon

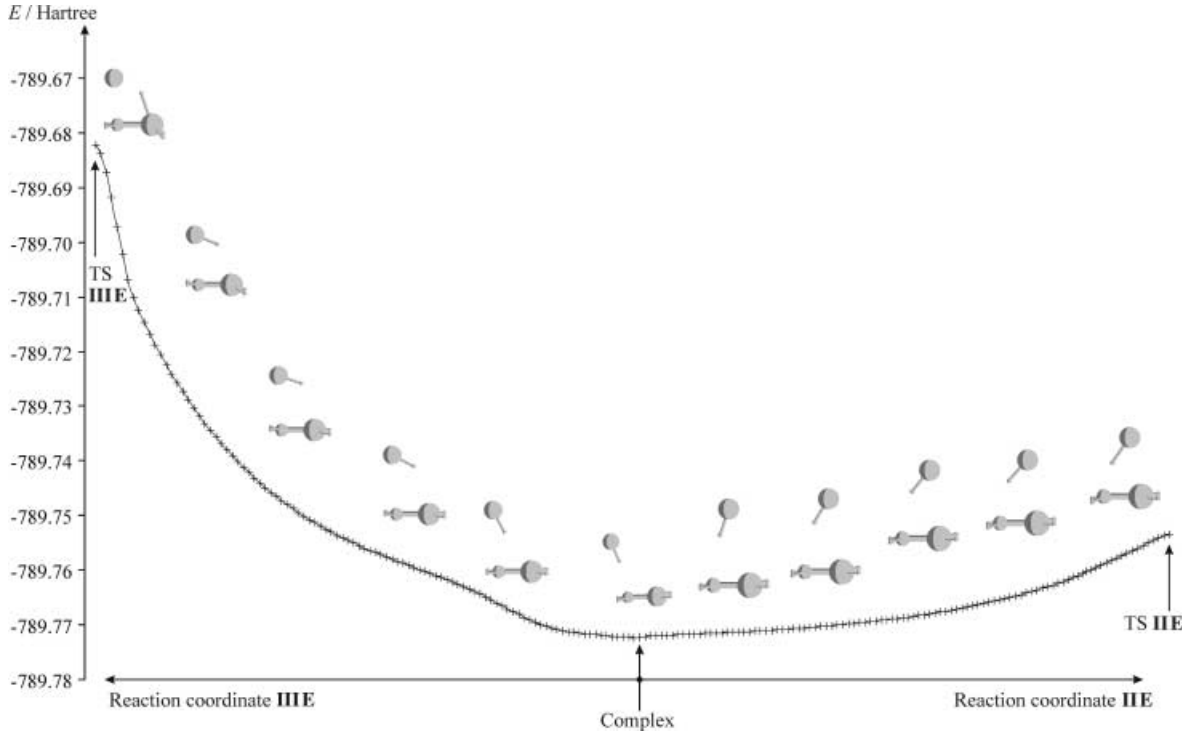

Figure 7. Intrinsic reaction coordinates of **IIE** and **IIIE** starting from the common initial complex.

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becomes strongly negative, compared with the charge distribution of the initial complex, while the other silicon is strongly positive. The charge separation of the hydrogen halide increases with a more negative halogen and a more positive hydrogen, but the total charge of the H–Y moiety does not change significantly. As a consequence, this stage of the reaction can be considered as a bond formation between the halogen atom and silicon.

In spite of the huge activation energies, the originally planar geometry of ethene is much less distorted in the transition state of **IVD** and **IVE** than in the analogous transition states of disilene. Both the moderate bond elongation and the shape of HOMO indicate that the C–C bond partially keeps its double bond character. The H–Y bond, however, is drastically elongated by 0.37 Å (HF) and 0.50 Å (HCl), and the hydrogen is closer to ethene than the halogen atom. All these facts suggest that the leading processes at this stage are the Y–H bond breaking and C–H bond formation. During this process the halogen atom becomes strongly negative (compared with the relatively positive halogen in the case of **ID** and **IE** reactions). Therefore this point of the reaction can also be interpreted as an ion-pair formation: hydrogen halide ionically dissociates in the transition state and yields a carbenium ion intermediate that evolves in the next step to the product. This explanation makes the huge activation energy of such reactions understandable: a large part of the energy is used in the dissociation of hydrogen. Indeed, the calculated energy necessary for the same bond elongation of HF and HCl is 45.25 and 45.61 kcal mol^{-1}, respectively (at the MP2/-311++G(d,p) level), which is about 90% of the total activation energy of **IVD** and **IVE**.

It is interesting to note that although the initial complexes of the reactions of disilene with hydrogen halides (**ID** and **IE**) are very similar to those of the corresponding reactions of ethene (**IVD** and **IVE**), the subsequent pathways selected are very different from each other; in the final step of the reactions **ID** and **IE**, the halogen as a nucleophile attacks a silicon to form four-membered cyclic transition states, while in **IVD** and **IVE**, heterolytic H–Y bond cleavage takes place to give the H–C bond in the transition state. This selectivity may be explained by the preferred orbital interaction in the final step. We can expect the stabilizing interaction between the π^* orbital and lone-pair orbital in the nucleophilic interaction in this step as found in the disilene + water reaction.[1b, d] Since disilene has a low-lying π^* orbital,[16] this interaction is actually effective in the reactions **ID** and **IE**, and this leads to the cyclic transition state found theoretically. On the other hand, in **IVD** and **IVE**, since ethene π^* orbital level is rather high, a similar interaction between ethene π^* and the lone-pair orbitals is less effective, and hence, the other pathway to form the hydrogen–carbon bond with heterolytic HY cleavage will be selected.

As predicted, the reactions of silene bear the special marks of **I** and **IV**. The energy and structure of the transition states along the two different directions of the HY addition are quite different (Figures 5 and 6). In **IIID** and **IIIE**, a huge activation energy is required, and the HY bond is elongated like in the reactions of **IVD** and **IVE**. On the other hand, the structure at the silicon atom is greatly bent with a formal lone electron pair, which forms the HOMO. This fact and the degree of the Si–C bond elongation mean that it resembles the reaction of **ID** and **IE**. In the reaction of **IID** and **IIE**, the activation energy is small, the structure of the highly positive silicon is almost planar, while the carbon side is only moderately bent (similarity to **ID** and **IE**). The Si–C distance is, however, closer to the double bond than to the single bond, and the shape of HOMO is a (deformed) π bond between the C and Si atoms (like in **IVD** and **IVE**).

The charge distribution of HF, in the reaction of **IID** and **IIID** resembles those of **ID** and **IVD**, respectively. Evidently, the halogen atom is more negative, and the hydrogen is less positive when they approach the silicon side of the substrate molecule. It can be inferred from the facts above that the mechanisms of the addition in **IID** and **ID** and also in **IIID** and **IVD** are similar. From this feature the transition state of HCl addition to silene is somewhat different. In both **IIE** and **IIIE** the hydrogen is definitely closer to the substrate than the chlorine. The H–Cl bond is strongly elongated in both cases (although in **IIIE** it is much longer than in **IIE**), and a considerable charge shift from silene to HCl and an additional charge separation between H and Cl can be observed. The negative charge of HCl in **IIIE** is extremely large, and even in the reaction of **IIE** it is about the same as in **IVE**. From these facts it may follow that the ionic intermediate model discussed above tends to compete with the bimolecular way in **IIE** (because of the enhanced acidity of HCl compared with the HF), although the thermodynamic profile of the reaction is close to **IE**. To prove this hypothesis, some trial calculations (using the MP2/6-311++G(d,p) level) were carried out with the highly acidic HBr for the transition state of the following reactions.

$H_2C{=}SiH_2 + HBr$ **IIF**

$H_2Si{=}CH_2 + HBr$ **IIIF**

The comparison of the transition state geometries of **IID–F** and **IIID–F** (Figure 8) proves that the four-membered ring shape, characteristic of the usual bimolecular addition, is strongly deformed with increasing acidity, the elongation of C=Si distance as well as the H–C and H–Si distance gradually decreases, while the H–Y bond length gradually increases,[17] and this indicates the change in the dominant process.

Final products: The geometry, charge distribution, and energy data of the final products are shown in Tables 1 and 2. We have not studied the structural and energy differences between the staggered and eclipsed forms, but we expect from previous experience that the rotation barrier at the newly formed X^1–X^2 single bond is small, and the staggered form is more stable. All the investigated reactions are exothermic. The product molecules are stable and demonstrate the expected geometric data. From the two possible isomer products in the reactions of silene, the halosilanes are more stable in agreement with the experimental evidence.

Conclusion

The investigated reactions **ID – E**, **IID – E**, **IIID – E**, and **IVD – E** can be characterized by two main thermodynamic profiles. The type in which the reagent molecule attacks a carbon atom is moderately exothermic with a high activation barrier. The second type in which the hydrogen halide attacks a silicon is strongly exothermic with a low activation energy. At the early stage of all the reactions a weakly bonded initial complex is found, which indicates that the initial step of all the reactions is an electrophilic attack of hydrogen. In our previous work on the water and alcohol addition to the same substrate molecules, we discovered both electrophilic and nucleophilic initial complexes. Considering the highly acidic character of HY hydrogen, we find the lack of nucleophilic reaction channels is reasonable. The geometry and charge distribution of the transition state of the reactions indicate two main classes of mechanisms. If silicon is attacked, the halogen – silicon bond formation precedes the H–Y bond breaking. If, however, carbon is attacked, the first step is always an ionic dissociation of hydrogen halide and a carbenium ion formation, which is stabilized in the final step of the reaction by the C–Y bond formation. Some preliminary calculations suggest, however, that with increasing acidity of the reagent the ionic mechanism will probably be dominant even in the attack of silicon. The reaction diagrams and proposed mechanisms explain the experimentally found regioselectivity well.

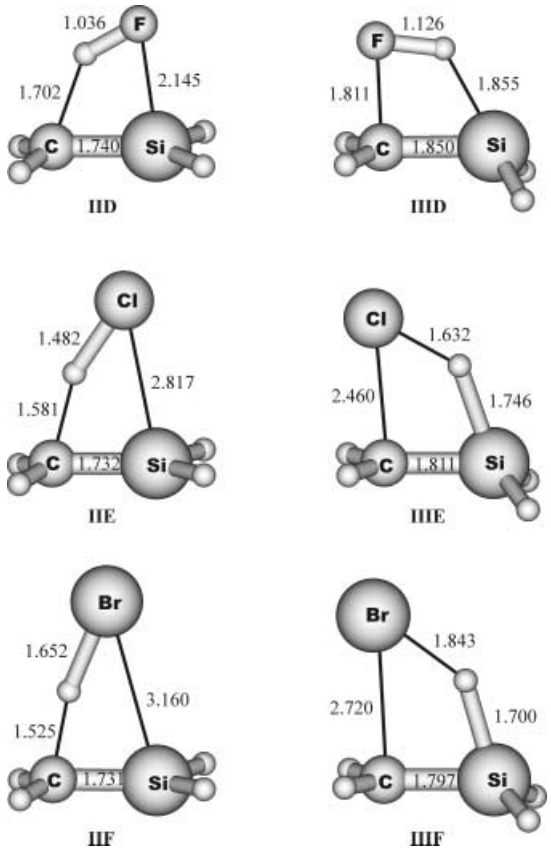

Figure 8. The optimized geometry of transition states of **IID – F** and **IIID – F** at the MP2/6-311++G(d,p) level.

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[18] All figures were made by using the MOLDEN program: G. Schaftenaar, MOLDEN 3.6, CMBI, University Nijmegen, Nijmegen (The Netherlands).

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