

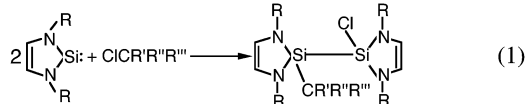
Theoretical Study of Halophilic Reactions of Stable Silylenes with Chloro- and Bromocarbons

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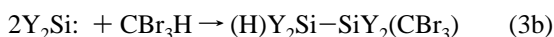
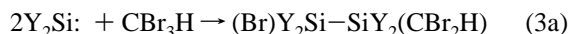
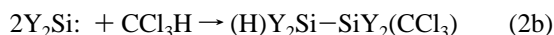
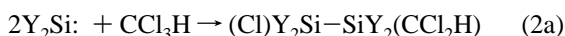
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Recently, West and co-workers reported some surprising reactions of the stable silylene¹ with chloro- and bromocarbons leading to disilanes.² In these reactions, cyclic diaminosilylene has been found to insert into a C–X (X = halogen) bond of a halocarbon. The silylene insertion reaction gives rise to a disilane that can consume another stable silylene molecule; see eq 1.



On the basis of the experimental findings, West and co-workers proposed one possible mechanism for the silylene insertion process: the stable silylene (1) interacts with a halocarbon to form a weak Lewis acid–base complex (2). This stage is followed by the formation of another acid–base adduct (3) with an additional external silylene. This adduct undergoes a 1,3-shift which leads to disilane formation (4); see Scheme 1. Obviously, these novel experiments left several questions unsolved, including the following: (a) What are the structures and energetics of the assumed intermediates and transition states (TSs) involved in the reaction? (b) Why do stable silylenes undergo carbon–halogen rather than carbon–hydrogen bond insertion? (c) What is the role of the Lewis acid–base complex in such a disilane formation reaction? We believe that quantum chemical calculations, together with experiment, are very useful in solving these and related problems.

Therefore, in the present paper, we use density functional theory (DFT)^{3–5} to investigate the potential energy surfaces and mechanisms of the following reactions:

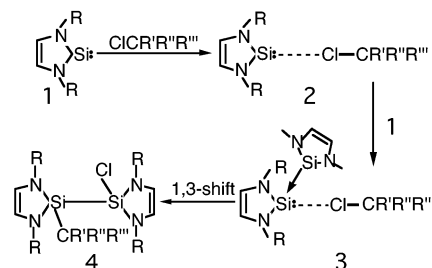


where Y₂Si: is the cyclic diaminosilylene.

Our theoretical findings suggest that these disilane formation reactions are highly exothermic, and both thermodynamic and kinetic factors are responsible for the observed preference for C–Cl (or C–Br) over C–H bond insertion.

The relative energies of the stationary points for eqs 2 and 3 based on the B3LYP/6-31G* level are collected in Table 1. The results are summarized in the schematic reaction profiles in Figure 1, and the calculated geometrical parameters for the stationary points are given in Figures A–D in the Supporting Information. The major conclusions drawn from the current study can be summarized as follows.⁶

Scheme 1



Scheme 2

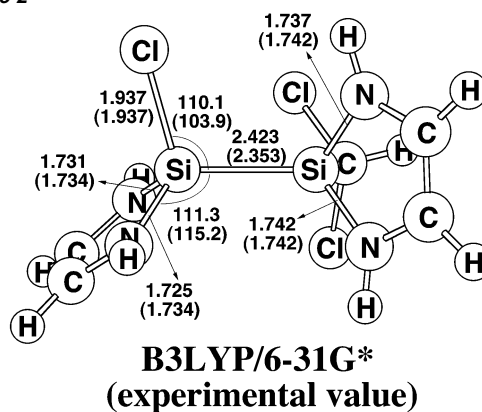


Table 1. Relative Energies (kcal/mol) for the Process of the Insertion of Cyclic Diaminosilylene into Halocarbons at the B3LYP/6-31G* Level^a

halocarbon	rea ^b	$\Delta E(\text{Int-1})^c$	$\Delta E(\text{TS-1})^c$	$\Delta E(\text{Int-2})^c$	$\Delta E(\text{TS-2})^c$	$\Delta H(\text{Pro})^c$
CHCl ₃ (Cl-attack)	0.0	-0.2554	+52.50	-48.31	-31.41	-56.02
CHBr ₃ (Br-attack)	0.0	-3.170	+45.65	-55.56	-43.59	-65.10
halocarbon	rea ^b	$\Delta E(\text{Int-1})^d$	$\Delta E(\text{TS-1})^d$	$\Delta E(\text{Int-2})^d$	$\Delta E(\text{TS-2})^d$	$\Delta H(\text{Pro}')^d$
CHCl ₃ (H-attack)	0.0	-0.2554	+54.78	-6.380	+25.05	-8.512
CHBr ₃ (H-attack)	0.0	-3.170	+44.70	-14.72	+15.38	-19.20

^a See Figure 1. ^b The energy of 2Y₂Si: + CX₃H (X = Cl and Br) is taken as reference. ^c The energy of **Int-1**, **TS-1**, **Int-2**, **TS-2**, and **Pro** relative to that of the corresponding reactants. ^d The energy of **Int-1'**, **TS-1'**, **Int-2'**, **TS-2'**, and **Pro'** relative to that of the corresponding reactants.

(1) Our theoretical investigations show that, in general, the reaction proceeds via two distinct pathways (Figure 1): (A) C–X bond insertion (i.e., halophilic reaction) and (B) C–H bond insertion (i.e., hydrogenphilic reaction). Both of these start from the same intermediate, **Int-1**. The first step of path A is the first silylene insertion into the C–X bond (**TS-1**) leading to the XY₂Si–CX₂H

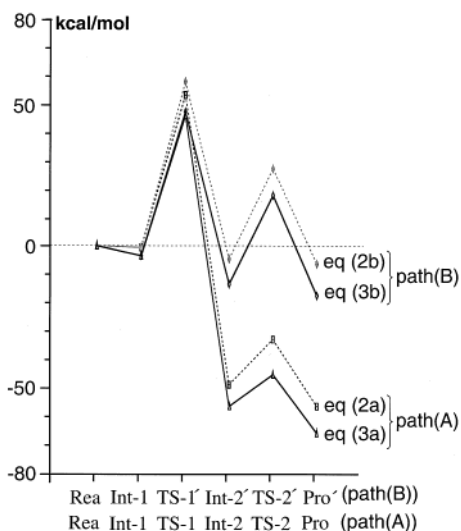


Figure 1. Potential energy surfaces for the reactions of cyclic diaminosilylene with CCl_3H (dashed line) and CBr_3H (plain line). The relative energies are taken from the B3LYP/6-31G* level as given in Table 1. For path A and path B, see the text.

molecule (**Int-2**). The second silylene is then inserted into the Si–X bond of $\text{XY}_2\text{Si}-\text{CX}_2\text{H}$ (**TS-2**), and subsequently Si–Si bond formation (i.e., $\text{XY}_2\text{Si}-\text{SiY}_2(\text{CX}_2\text{H})$; **Pro**) takes place. In path B, the first silylene is inserted into the C–H bond (**TS-1'**), followed by Si–C bond formation to yield $\text{HY}_2\text{Si}-\text{CX}_3$ (**Int-2'**). The 1,2-H shifted product (i.e., $\text{HY}_2\text{Si}-\text{SiY}_2\text{X}_3$; **Pro'**) then forms via insertion of the second silylene into the Si–H bond of $\text{HY}_2\text{Si}-\text{CX}_3$ (**TS-2'**).

(2) It is reasonable to expect that the first step in the reaction of a silylene with a halocarbon is the formation of a precursor complex (**Int-1**), which then undergoes a 1,2-shift resulting in a halosilane (**Int-2** or **Int-2'**). These precursor complexes were confirmed to have no imaginary frequency, demonstrating that they are true minima on the potential energy surfaces. In fact, these intermediates (**Int-1**) correspond to donor–acceptor complexes forming $\text{Y}_2\text{Si}:-\cdots-\text{XCX}_2\text{H}$ ($\text{X} = \text{Cl}$ and Br) structures, in which the halogen lone pairs donate electrons to the silylene empty p-orbital. Additionally, B3LYP calculations predict that they all have a small complex stabilization energy of 0.3–3.1 kcal/mol, which is consistent with the extremely long Si–X bond distances (3.28–3.81 Å) in these complexes. This strongly implies that the silylene–halocarbon complexes are unlikely to be isolated experimentally at room temperature.

(3) As seen in Figure 1 and Table 1, it is clear that the preference of the C–X (path A) over C–H bond insertion (path B) is a result of the thermodynamic factor. On one hand, it is apparent from Figure 1 that the energy of the **TS-2** is below the energy of the corresponding reactants, while that of **TS-2'** is higher than that of the corresponding reactants. On the other hand, the present calculations predict that the overall enthalpies for the insertion of cyclic diaminosilylene into $\text{Cl}-\text{CCl}_2\text{H}$ and $\text{H}-\text{CCl}_3$ are –56 (path A) and –8.5 (path B) kcal/mol, respectively. Similarly, the overall enthalpies for $\text{Br}-\text{CBr}_2\text{H}$ and $\text{H}-\text{CBr}_3$ bond insertions are –65 (path A) and –19 (path B) kcal/mol, respectively. As a result, once

the C–X bond insertion barrier is surmounted, the additional external silylene readily undergoes insertion into the Si–X bond of halosilane (**Int-2**) in a concerted fashion. Consequently, path A (halophilic reaction) is favored over path B (hydrogenphilic reaction) from the thermodynamic point of view.⁷ This is in accordance with experimental observations.²

(4) Again, as one can see in Table 1, stable silylenes prefer to insert into a C–Br rather than a C–Cl bond because the energy barrier to insertion is lower, and the reaction is more exothermic, providing that the reaction conditions remain the same.

(5) Our model calculations demonstrate that, from the thermodynamic viewpoint, it seems reasonable to dismiss the involvement of Lewis acid–base complexes between silylene and halocarbon. The reason for this is that they do not play a role in the overall energetics of the silylene insertion chemistry into halocarbons, and perhaps the same can be said of their importance in defining the kinetics. Accordingly, on the basis of the present model calculations, one may then conclude that the acid–base complex mechanism proposed by West et al. (Scheme 1)² is not appropriate to describe the disilane formation reaction.

Future work along this line is in progress and will be published elsewhere.

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Supporting Information Available: B3LYP/6-31G* geometries (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (3) The geometries and energetics of the stationary points on the potential energy surface of Figure 1 have been calculated with the B3LYP method (see refs 4 and 5) in conjunction with the 6-31G* basis set. All of the stationary points have been positively identified as equilibrium structures (the number of imaginary frequency (NIMAG = 0) or transition states (NIMAG = 1)). Relative energies are thus corrected for vibrational zero-point energies (ZPE, not scaled). All calculations were performed using the Gaussian 94 package (see ref 5).
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- (6) As one can see in Scheme 2, the computed structure of the disilane compound agrees well with the available experimental data. Thus, it is believed that the present models with the current method (B3LYP/6-31G*) employed in this study should provide reliable information for the discussion of the reaction mechanism.
- (7) Bond dissociation energetics (kJ/mol): C–H 338, Si–H 299; C–Cl 397, Si–Cl 406; C–Br 280, Si–Br 368. See: Lide, D. R.; Frederikse, H. P. R. *CRC Handbook of Chemistry and Physics*; CRC Press: New York, 1998; pp 9–51.

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