

## Investigation of Reaction Paths from Si + CH<sub>4</sub> to C + SiH<sub>4</sub> and from Si + CH<sub>3</sub>F to C + SiH<sub>3</sub>F: Intrinsic Reaction Coordinate Studies

Han-Gook Cho

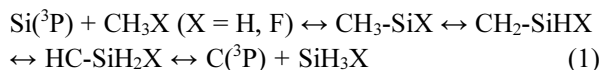
Department of Chemistry, Incheon National University, Incheon 22012, Korea.

E-mail: hgc@incheon.ac.kr

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In this study the reaction paths from Si + CH<sub>4</sub> to C + SiH<sub>4</sub> and from Si + CH<sub>3</sub>F to C + SiH<sub>3</sub>F (1) have been investigated by intrinsic reaction coordinate (IRC) calculations.<sup>1</sup> The previously reported products (CH<sub>3</sub>-SiH, CH<sub>2</sub>-SiH<sub>2</sub>, HC-SiH<sub>3</sub>, CH<sub>3</sub>-SiF, and CH<sub>2</sub>-SiHF)<sup>2-4</sup> are the viable energy minima along the reaction paths, and the transition states between the products are the proper saddle points in the triplet potential surface. Therefore, a considerable amount of activation energy is needed for each steps to occur. In contrast, the conversion from HC-SiH<sub>3</sub> to energetically high [C + SiH<sub>4</sub>] is barrierless, explaining recent provision of the silyl carbene in reaction of laser-ablated C.



Si is a metalloid that readily donates or shares its four valence electrons to form chemical bonds, combining with many other element to form various compounds.<sup>5</sup> Unlike carbon it sometimes accept additional electrons to form hypervalent products with five or six bonds.<sup>6</sup> Recent matrix spectroscopic studies have shown that silicon, like transition-metals, readily undergoes C-X (X = H, halogen) insertion and following X migration from C to Si in reactions with methane and halomethanes, generating small methyl silylenes, silaethenes, and silyl carbenes without a trace of hypervalent products.<sup>7</sup>

Maier *et al.* have identified CH<sub>3</sub>-SiH and CH<sub>2</sub>=SiH<sub>2</sub> in reactions of Si + CH<sub>4</sub> from the matrix spectra and also proposed a reaction path (initial C-H insertion by Si and following H migration),<sup>2</sup> which is in fact similar to that for reaction of a transition-metal with methane.<sup>7,8</sup> They have later reported production of halogenated derivatives (CH<sub>3</sub>-SiX and CH<sub>2</sub>=SiHX) in reactions of Si with methyl halides.<sup>3</sup> Schreiner *et al.* have observed HC-SiH<sub>3</sub> from matrix ESR and infrared spectra in reaction of C(<sup>3</sup>P) with SiH<sub>4</sub> and the ESR hyperfine structures indicate that the silyl carbene

owns a triplet ground state like other carbenes (CX<sub>2</sub>, X = H, halogen).<sup>4</sup> Cho and Andrews have shown that the silaethene is the primary product in reactions of dihalomethanes and the silyl carbenes in reactions of tri- and tetrahalomethanes.<sup>7</sup>

These Si bearing products from its s<sup>2</sup>p<sup>2</sup> electron configuration are in fact similar to those from Ti (s<sup>2</sup>d<sup>2</sup>) reactions, but the Ti methylidyne (XC≡TiX<sub>3</sub>) own a much stronger C-Ti bond by effective electron donation from C to Ti's low lying d-orbitals.<sup>2-4,7,8</sup> The previous studies have shown that Ti also generates CH<sub>3</sub>-MH and CH<sub>2</sub>=MH<sub>2</sub> in reactions with CH<sub>4</sub>, but they produce CH<sub>2</sub>=MX<sub>2</sub> with CH<sub>2</sub>X<sub>2</sub> and triplet methylidyne (HC≡CX<sub>3</sub> and XC≡MX<sub>3</sub>) with tri- and tetrahalomethanes.<sup>7,8</sup> Substitution of H with halogen increases the stability of the higher oxidation-state compounds due to the stability of M-X bond.

Density functional theory (DFT) calculations<sup>9</sup> were carried out for the Si bearing products and transition states using the Gaussian 09 package,<sup>10</sup> the B3LYP hybrid density functional,<sup>11</sup> and the 6-311++G(3df, 3pd) basis sets for H, C, F, and Si.<sup>12</sup> Geometries were fully relaxed during optimization, and the optimized geometry was confirmed by vibrational analysis, all real frequencies for a stable conformation and a single imaginary frequency for a transition state. Each transition state was linked to its reactant and product by intrinsic reaction coordinate (IRC) calculation.<sup>1</sup> Natural bond orbital (NBO) calculations<sup>13</sup> were also done to examine the bond properties of the Si compounds and electron-donations between the MO's. The vibrational frequencies were calculated analytically. In the calculation of binding energy for a Si product, the zero-point energy is included.

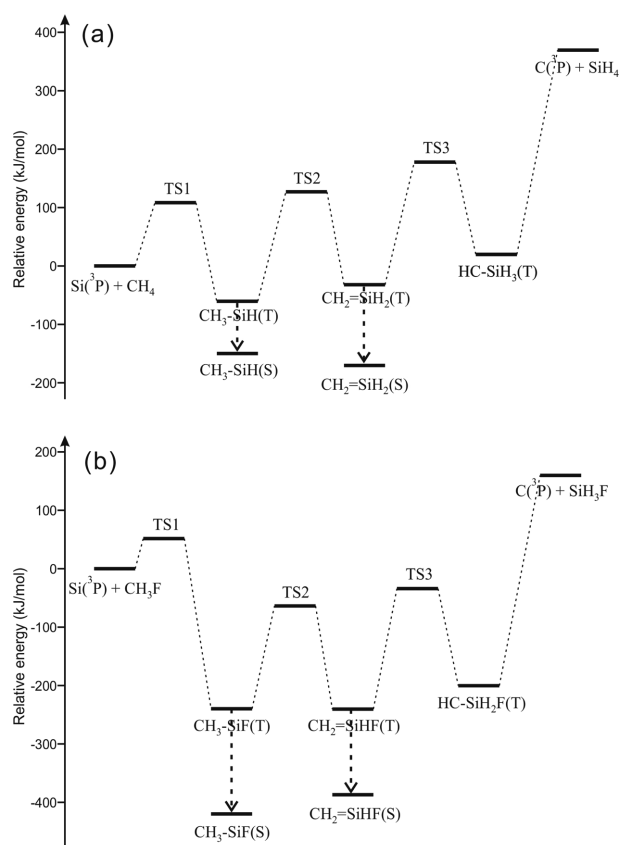
Due to the law of spin conservation and the ground states of C and Si (<sup>3</sup>P), these Si reactions most probably occur in a triplet potential surface. Fig. 1 illustrates the energies of the products and transition states relative to the reactants

[Si(<sup>3</sup>P) + CH<sub>4</sub> and Si(<sup>3</sup>P) + CH<sub>3</sub>F]. These results reveal that both the C-H and C-F insertion reactions by atomic Si have to go over a considerable barrier, requiring extra photon energy to provide enough kinetic energy to the reactants in a cold matrix. It is consistent with the observed results that the Si products were generated during photolysis after original deposition.<sup>2-4</sup>

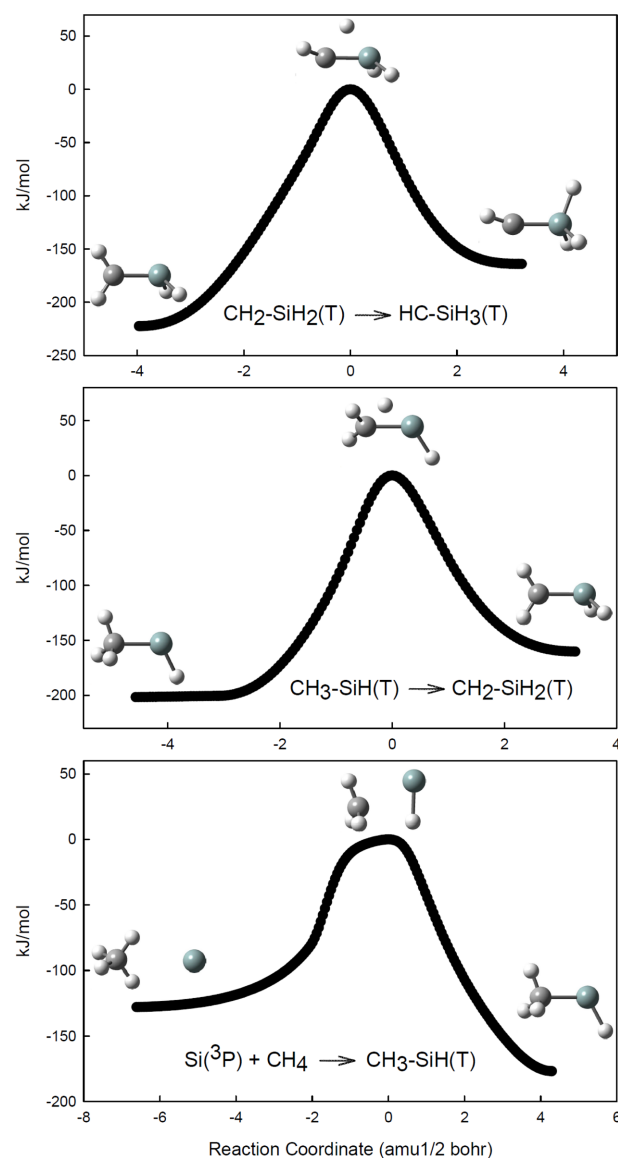
TS1, TS2, and TS3 in the methane reaction are considerably higher than the reactants [107, 126, and 177 kJ/mol higher than Si(<sup>3</sup>P) + CH<sub>4</sub> as shown in Fig. 1(a)], indicating that the reaction becomes increasingly more difficult as moving toward its end [SiH<sub>4</sub> + C(<sup>3</sup>P)]. The previous studies have also shown that while the insertion compound (CH<sub>3</sub>-SiH) is the primary reaction product on UV photolysis (λ = 185 or 254 nm), and the silaethane is detected after additional UV irradiation (λ = 254 nm), but HC-SiH<sub>3</sub> is not observed.<sup>2</sup> The silyl carbene is provided later in reaction of SiH<sub>4</sub> + C(<sup>3</sup>P),<sup>4</sup> which is 372 kJ/mol higher in energy than Si(<sup>3</sup>P) + CH<sub>4</sub>. This reaction [SiH<sub>4</sub> + C(<sup>3</sup>P) → HC-

SiH<sub>3</sub>(T)] is evidently barrierless as shown in Fig. 1(a) [and Fig. 4(a)] while the next reaction step from HC-SiH<sub>3</sub>(T) to CH<sub>2</sub>-SiH<sub>2</sub>(T) requires a substantial activation energy (151 kJ/mol), leading to provision of the silyl carbene (HC-SiH<sub>3</sub>).<sup>4</sup>

Inter-system crossing is supposed to take place once CH<sub>3</sub>-SiH and CH<sub>2</sub>=SiH are generated; the singlet methyl silylene and silaethene are 153 and 171 kJ/mol more stable than the reactants. Maier *et al.* have also reported that the observed vibrational characteristics of the methyl silylene and silaethene correlate with the predicted values for their



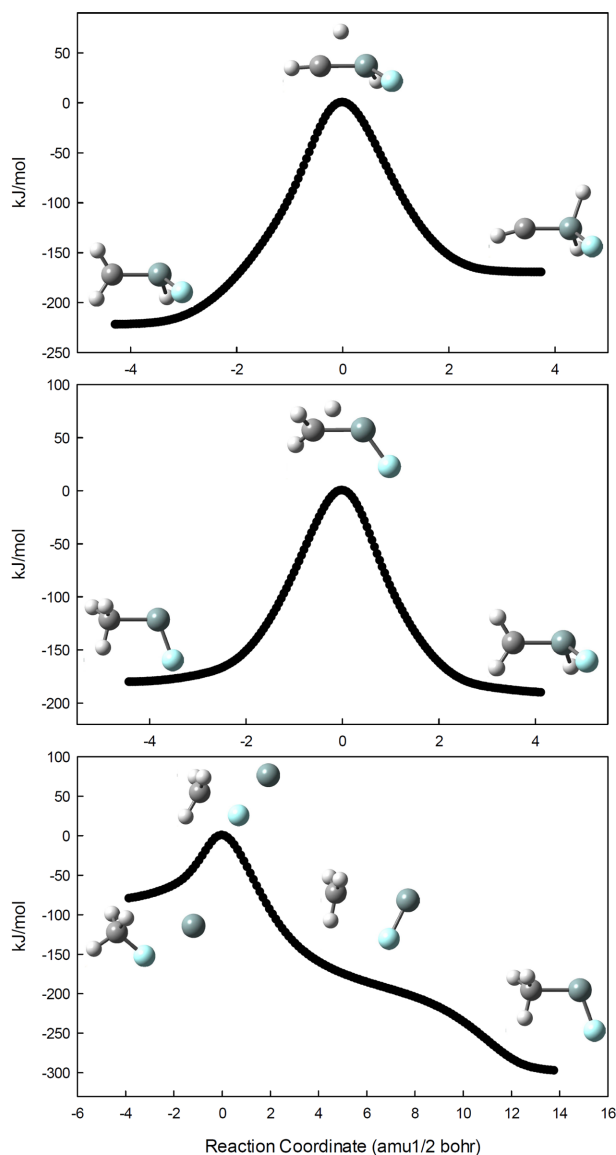
**Figure 1.** Energies of the products and transition states relative to Si(<sup>3</sup>P) + CH<sub>4</sub> (a) and those of the monofluorided analogues to Si(<sup>3</sup>P) + CH<sub>3</sub>F (b) calculated at the the B3LYP/6-311++G (3df, 3pd) level of theory. Each transition state is confirmed by linking it to its reactant and product by intrinsic reaction coordinate (IRC) calculations as shown in Figs. 2-4.



**Figure 2.** Energy variations in the reaction steps from Si(<sup>3</sup>P) + CH<sub>4</sub> → HC-SiH<sub>3</sub>(T). Intrinsic reaction coordinate (IRC) calculations are done for the transition states at the level of B3LYP/6-311++G(3df, 3pd), showing that the reported silicon bearing products are the energy minima in the triplet potential surface.

singlet states.<sup>2</sup> On the other hand, all our attempts to optimize the geometry of singlet HC-SiH<sub>3</sub> ended up with the structure of CH<sub>2</sub>=SiH<sub>2</sub>, suggesting that singlet HC-SiH<sub>3</sub> is not a meaningful energy minimum. The observed vibrational characteristics and ESR hyperfine structures also correlate with those predicted for triplet HC-SiH<sub>3</sub>.<sup>4</sup>

In reaction of Si(<sup>3</sup>P) + CH<sub>3</sub>F, TS1, TS2, and TS3 are considerably lower than those in the Si(<sup>3</sup>P) + CH<sub>4</sub> system, 56, -65, -37 kJ/mol higher than the reactants [Fig. 1(b)]. Therefore, C-F insertion by Si to form CH<sub>3</sub>-SiF is expected to be easier, but the following conversions to CH<sub>2</sub>-SiHF and to

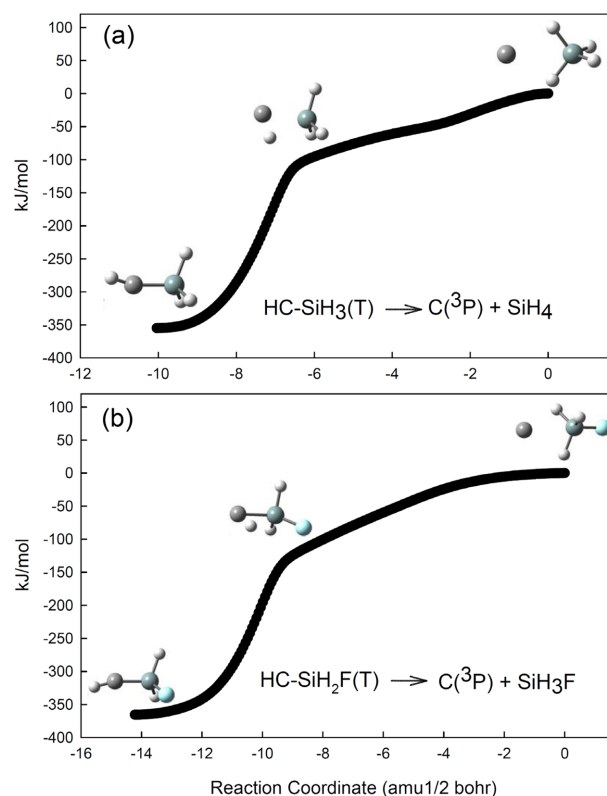


**Figure 3.** Energy variations in the reaction steps from Si(<sup>3</sup>P) + CH<sub>3</sub>F → HC-SiH<sub>2</sub>F(T). Intrinsic reaction coordinate (IRC) calculations are done for the transition states at the level of B3LYP/6-311++G(3df,3pd), showing that the reported silicon bearing products are the energy minima in the triplet potential surface.

HC-SiH<sub>2</sub>F to be more difficult. The F bearing Si products are relatively more stable than the corresponding analogues in the Si(<sup>3</sup>P) + CH<sub>4</sub> system due to the strong Si-F bond (540 kJ/mol).<sup>14</sup> Maier *et al.* have observed a Si adduct (CH<sub>3</sub>F...Si) in the original deposition spectrum, which easily converts to CH<sub>3</sub>-SiF by short UV or visible photolysis.<sup>3</sup> CH<sub>2</sub>=SiHF was observed later on much longer irradiation with λ = 366 nm.

The fluorosilyl carbene (HC-SiH<sub>2</sub>F), which is expected to be more difficult to provide as shown in Fig. 1(b), has not been reported. However, the present results indicate that provision of HC-SiH<sub>2</sub>F is probably possible via reaction of C(<sup>3</sup>P) + SiH<sub>3</sub>F, parallel to the case of HC-SiH<sub>3</sub>, where the silyl carbene is produced in reaction of laser-ablated graphite plume with a SiH<sub>4</sub>/Ar gas mixture on the surface of a cold window (1-12 K) by Schreiner *et al.*<sup>4</sup> As shown in Figs. 1(b) and 4(b), the Si-H insertion reaction by C is apparently barrierless and continuous downhill to HC-SiH<sub>2</sub>F, while the reaction from HC-SiH<sub>2</sub>F to CH<sub>2</sub>-SiHF has to go over a considerable barrier (161 kJ/mol), making the fluorosilyl carbene a stable conformation.

CH<sub>3</sub>-SiF and CH<sub>2</sub>=SiHF are also expected to undergo system crossing to their singlet ground states, which are



**Figure 4.** Energy variations in reactions from HC-SiH<sub>3</sub> to C(<sup>3</sup>P) + SiH<sub>4</sub> (a) and from HC-SiH<sub>2</sub>F to C(<sup>3</sup>P) + SiH<sub>3</sub>F (b). These IRC calculation results show that they are barrierless, uphill reactions to the energetically high products.

182 and 134 kJ/mol more stable than the triplet counter parts. Maier *et al.* have also reported that the observed vibrational characteristics of the fluorided products correlate with the computed values for the singlet species.<sup>3</sup> The silyl carbene, on the other hand, has a triplet ground state. Our attempts for geometry optimization of singlet HC-SiH<sub>2</sub>F all lead to the structure of singlet CH<sub>2</sub>=SiHF, indicating that this singlet fluorosilyl carbene is also not a meaningful energy minimum.

*Figs. 2 and 3* illustrate our IRC computation results for the reaction steps in the course of Si(<sup>3</sup>P) + CH<sub>4</sub> → HC-SiH<sub>3</sub>(T) and those for the fluorided counterparts, showing that each step is a smooth conversion over its barrier. *Fig. 4* shows the energy variations in conversions of HC-SiH<sub>3</sub> to C(<sup>3</sup>P) + SiH<sub>4</sub> (a) and HC-SiH<sub>2</sub>F to C(<sup>3</sup>P) + SiH<sub>3</sub>F (b), both of which are barrierless and continuous uphill. *Figs. 2-4* also show that the product of a previous reaction step is the reactant of the next reaction step, the entire reaction path being a series of smooth conversions from one to another product. This suggests that the generally accepted reaction mechanism (initial C-H or C-F insertion and subsequent H migrations) is most probably the true reaction course, which connects the saddle points in the triplet potential surface.

The structures of triplet CH<sub>3</sub>-SiH and CH<sub>3</sub>-SiF in *Figs. S1 and S2* are similar to those of the singlet counterparts,<sup>2,3</sup> whereas triplet CH<sub>2</sub>-SiH<sub>2</sub> and CH<sub>2</sub>-SiHF own non-planar structures due to lack of C-Si  $\pi$ -bond (natural C-Si bond orders<sup>13</sup> 0.99 and 0.98), which contrasts the more usual planar or near planar geometry in the singlet states.<sup>2,3,7,8</sup> The structure of triplet HC-SiH<sub>3</sub> is almost identical to the reported structure,<sup>4</sup> carrying a bent HCSi moiety (160.5°) due to the unpaired electrons staying on C. Other carbenes also have a bent structure (e.g. 135.2° for CH<sub>2</sub> at the same level of theory). The non-bonding electrons reportedly have considerable contribution to the C-Si bond ( $\pi$  characters), leading to a shorter C-Si bond (*Figs. S1 and S2*).<sup>7</sup>

In conclusion, the Si bearing products and transition states in the triplet reaction paths from Si(<sup>3</sup>P) + CH<sub>4</sub> to C(<sup>3</sup>P) + SiH<sub>4</sub> and from Si(<sup>3</sup>P) + CH<sub>3</sub>F to C(<sup>3</sup>P) + SiH<sub>3</sub>F have been examined. Each transition state is linked by IRC computation to its reactant and product, confirming that the reaction path is a series of smooth conversions from one to another reported product.<sup>2-4</sup> Unlike other reaction steps, conversion of silyl carbene to C(<sup>3</sup>P) + SiH<sub>3</sub>X (X = H or F) is a continuous, barrierless uphill. Therefore, the unreported fluorosilyl carbene may be prepared in reaction of atomic C with SiH<sub>3</sub>F, similar to the case of HC-SiH<sub>3</sub>.<sup>4</sup> The silyl carbenes have a triplet ground state, leading to a bent HCSi moiety. The triplet methyl silylene and silaethenes with

unusual non-planar structures are supposed to undergo a system crossing to the singlet ground state, whose vibrational characters correlate with the experimentally observed values.<sup>2-4</sup>

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**Supporting Information.** *Figs. S1 and S2* showing the molecular structures of methyl silylene, silaethene, and silyl carbene and the involved transition states in reaction paths of Si(<sup>3</sup>P) + CH<sub>4</sub> → C(<sup>3</sup>P) + SiH<sub>4</sub> and Si(<sup>3</sup>P) + CH<sub>3</sub>F → C(<sup>3</sup>P) + SiH<sub>3</sub>F.

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