

Investigation of Reaction Paths from Si + CH₄ to C + SiH₄ and from Si + CH₃F to C + SiH₃F: Intrinsic Reaction Coordinate Studies

Han-Gook Cho

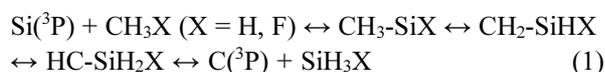
Department of Chemistry, Incheon National University, Incheon 22012, Korea.

E-mail: hgc@incheon.ac.kr

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In this study the reaction paths from Si + CH₄ to C + SiH₄ and from Si + CH₃F to C + SiH₃F (1) have been investigated by intrinsic reaction coordinate (IRC) calculations.¹ The previously reported products (CH₃-SiH, CH₂-SiH₂, HC-SiH₃, CH₃-SiF, and CH₂-SiHF)²⁻⁴ 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-SiH₃ to energetically high [C + SiH₄] 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.⁵ Unlike carbon it sometimes accept additional electrons to form hypervalent products with five or six bonds.⁶ 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.⁷

Maier *et al.* have identified CH₃-SiH and CH₂=SiH₂ in reactions of Si + CH₄ from the matrix spectra and also proposed a reaction path (initial C-H insertion by Si and following H migration),² which is in fact similar to that for reaction of a transition-metal with methane.^{7,8} They have later reported production of halogenated derivatives (CH₃-SiX and CH₂=SiHX) in reactions of Si with methyl halides.³ Schreiner *et al.* have observed HC-SiH₃ from matrix ESR and infrared spectra in reaction of C(³P) with SiH₄ and the ESR hyperfine structures indicate that the silyl carbene

owns a triplet ground state like other carbenes (CX₂, X = H, halogen).⁴ 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.⁷

These Si bearing products from its s²p² electron configuration are in fact similar to those from Ti (s²d²) reactions, but the Ti methylidyne (XC≡TiX₃) own a much stronger C-Ti bond by effective electron donation from C to Ti's low lying d-orbitals.^{2-4,7,8} The previous studies have shown that Ti also generates CH₃-MH and CH₂=MH₂ in reactions with CH₄, but they produce CH₂=MX₂ with CH₂X₂ and triplet methylidyne (HC≡CX₃ and XC≡MX₃) with tri- and tetrahalomethanes.^{7,8} 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) calculations⁹ were carried out for the Si bearing products and transition states using the Gaussian 09 package,¹⁰ the B3LYP hybrid density functional,¹¹ and the 6-311++G(3df, 3pd) basis sets for H, C, F, and Si.¹² 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.¹ Natural bond orbital (NBO) calculations¹³ 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 (³P), 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(³P) + CH₄ and Si(³P) + CH₃F]. 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.²⁻⁴

TS1, TS2, and TS3 in the methane reaction are considerably higher than the reactants [107, 126, and 177 kJ/mol higher than Si(³P) + CH₄ as shown in Fig. 1(a)], indicating that the reaction becomes increasingly more difficult as moving toward its end [SiH₄ + C(³P)]. The previous studies have also shown that while the insertion compound (CH₃-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-SiH₃ is not observed.² The silyl carbene is provided later in reaction of SiH₄ + C(³P),⁴ which is 372 kJ/mol higher in energy than Si(³P) + CH₄. This reaction [SiH₄ + C(³P) → HC-

SiH₃(T)] is evidently barrierless as shown in Fig. 1(a) [and Fig. 4(a)] while the next reaction step from HC-SiH₃(T) to CH₂-SiH₂(T) requires a substantial activation energy (151 kJ/mol), leading to provision of the silyl carbene (HC-SiH₃).⁴

Inter-system crossing is supposed to take place once CH₃-SiH and CH₂=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

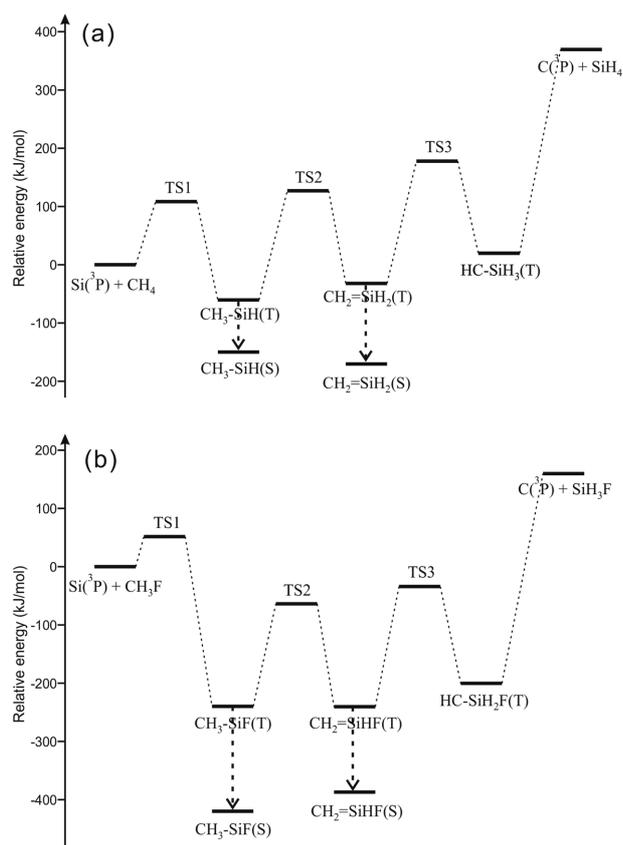


Figure 1. Energies of the products and transition states relative to Si(³P) + CH₄ (a) and those of the monofluorided analogues to Si(³P) + CH₃F (b) calculated at the the B3LYP/6-311++G (3df, 3pd) level of theory. Each transition state is confirmed by linking it to its reactant and product by intrinsic reaction coordinate (IRC) calculations as shown in Figs. 2-4.

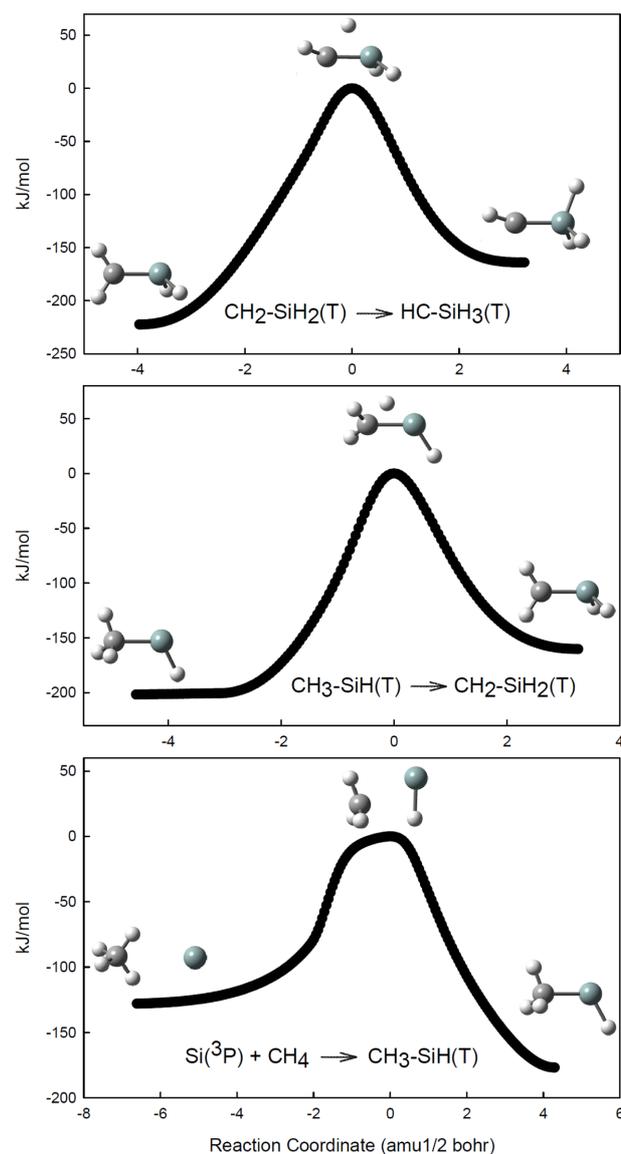


Figure 2. Energy variations in the reaction steps from Si(³P) + CH₄ → HC-SiH₃(T). Intrinsic reaction coordinate (IRC) calculations are done for the transition states at the level of B3LYP/6-311++G(3df, 3pd), showing that the reported silicon bearing products are the energy minima in the triplet potential surface.

singlet states.² On the other hand, all our attempts to optimize the geometry of singlet HC-SiH₃ ended up with the structure of CH₂=SiH₂, suggesting that singlet HC-SiH₃ is not a meaningful energy minimum. The observed vibrational characteristics and ESR hyperfine structures also correlate with those predicted for triplet HC-SiH₃.⁴

In reaction of Si(³P) + CH₃F, TS1, TS2, and TS3 are considerably lower than those in the Si(³P) + CH₄ system, 56, -65, -37 kJ/mol higher than the reactants [Fig. 1(b)]. Therefore, C-F insertion by Si to form CH₃-SiF is expected to be easier, but the following conversions to CH₂-SiHF and to

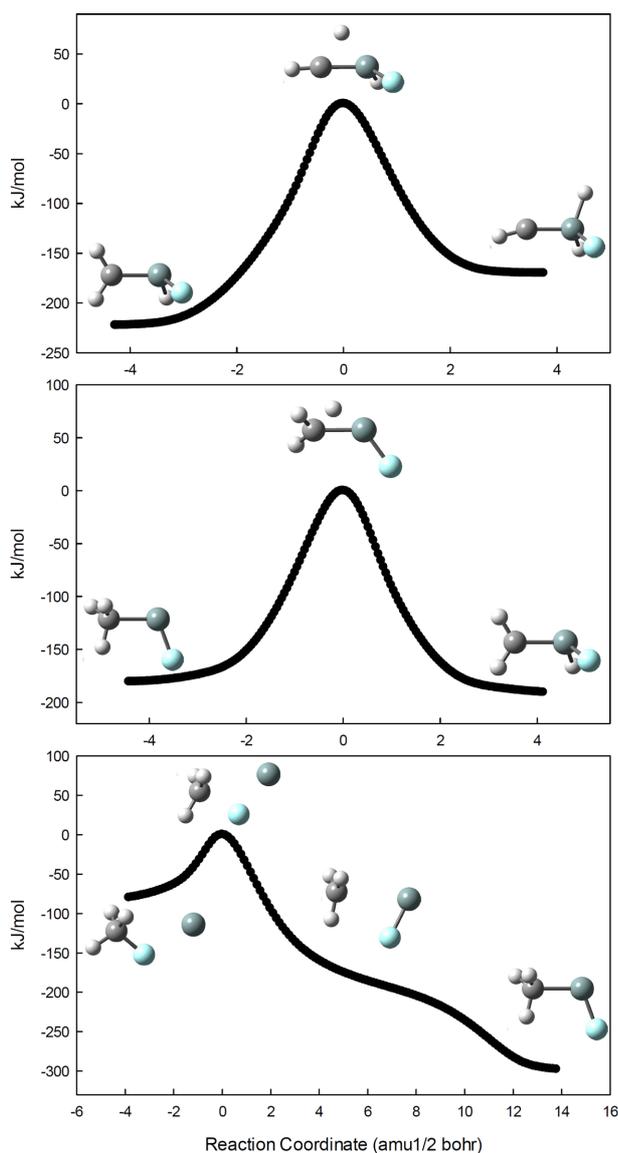


Figure 3. Energy variations in the reaction steps from Si(³P) + CH₃F → HC-SiH₂F(T). Intrinsic reaction coordinate (IRC) calculations are done for the transition states at the level of B3LYP/6-311++G(3df,3pd), showing that the reported silicon bearing products are the energy minima in the triplet potential surface.

HC-SiH₂F to be more difficult. The F bearing Si products are relatively more stable than the corresponding analogues in the Si(³P) + CH₄ system due to the strong Si-F bond (540 kJ/mol).¹⁴ Maier *et al.* have observed a Si adduct (CH₃F...Si) in the original deposition spectrum, which easily converts to CH₃-SiF by short UV or visible photolysis.³ CH₂=SiHF was observed later on much longer irradiation with λ = 366 nm.

The fluorosilyl carbene (HC-SiH₂F), 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-SiH₂F is probably possible via reaction of C(³P) + SiH₃F, parallel to the case of HC-SiH₃, where the silyl carbene is produced in reaction of laser-ablated graphite plume with a SiH₄/Ar gas mixture on the surface of a cold window (1-12 K) by Schreiner *et al.*⁴ As shown in Figs. 1(b) and 4(b), the Si-H insertion reaction by C is apparently barrierless and continuous downhill to HC-SiH₂F, while the reaction from HC-SiH₂F to CH₂-SiHF has to go over a considerable barrier (161 kJ/mol), making the fluorosilyl carbene a stable conformation.

CH₃-SiF and CH₂=SiHF are also expected to undergo system crossing to their singlet ground states, which are

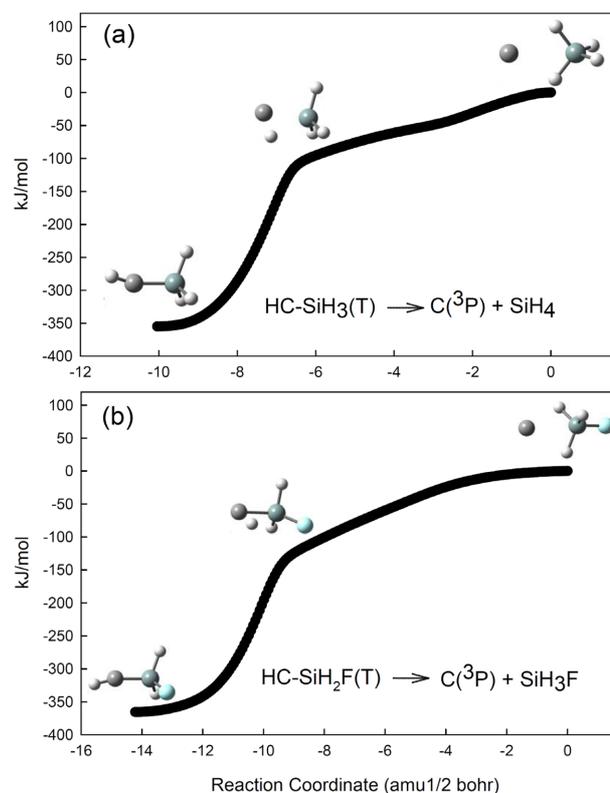


Figure 4. Energy variations in reactions from HC-SiH₃ to C(³P) + SiH₄ (a) and from HC-SiH₂F to C(³P) + SiH₃F (b). These IRC calculation results show that they are barrierless, uphill reactions to the energetically high products.

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.³ The silyl carbene, on the other hand, has a triplet ground state. Our attempts for geometry optimization of singlet HC-SiH₂F all lead to the structure of singlet CH₂=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(³P) + CH₄ → HC-SiH₃(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-SiH₃ to C(³P) + SiH₄ (a) and HC-SiH₂F to C(³P) + SiH₃F (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 CH₃-SiH and CH₃-SiF in *Figs. S1 and S2* are similar to those of the singlet counterparts,^{2,3} whereas triplet CH₂-SiH₂ and CH₂-SiHF own non-planar structures due to lack of C-Si π-bond (natural C-Si bond orders¹³ 0.99 and 0.98), which contrasts the more usual planar or near planar geometry in the singlet states.^{2,3,7,8} The structure of triplet HC-SiH₃ is almost identical to the reported structure,⁴ 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 CH₂ at the same level of theory). The non-bonding electrons reportedly have considerable contribution to the C-Si bond (π characters), leading to a shorter C-Si bond (*Figs. S1 and S2*).⁷

In conclusion, the Si bearing products and transition states in the triplet reaction paths from Si(³P) + CH₄ to C(³P) + SiH₄ and from Si(³P) + CH₃F to C(³P) + SiH₃F 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.²⁻⁴ Unlike other reaction steps, conversion of silyl carbene to C(³P) + SiH₃X (X = H or F) is a continuous, barrierless uphill. Therefore, the unreported fluorosilyl carbene may be prepared in reaction of atomic C with SiH₃F, similar to the case of HC-SiH₃.⁴ 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.²⁻⁴

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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(³P) + CH₄ → C(³P) + SiH₄ and Si(³P) + CH₃F → C(³P) + SiH₃F.

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