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Ab initio Chemical Kinetics of the Isobutene + SiH₃ Reaction

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ABSTRACT

The detailed kinetic mechanism between isobutene and SiH₃ radicals was investigated theoretically using the composite electronic structure method CBS-QB3 in conjugated with the Rice-Ramsperger-Kassel-Marcus based master equation (RRKM-ME) rate modeling. The study reveals that the title reaction proceeds through two primary pathways: (i) addition of SiH_3 to the double bond and (ii) H-abstraction by SiH₃, leading to various products. The addition pathway forms two primary products, P3 and P4. The H-abstraction pathway results in two product channels, P1 + SiH₄ and P2 + SiH₄. Among these, the adduct P3 is identified as the most thermodynamically and kinetically favorable intermediate at T < 900 K. However, at T > 900 K, **P1** and **P4** gain prominence. Pressure effect analysis (at P = 7.6 - 76000 Torr) shows that pressure has no significant influence on the reaction mechanism. The branching ratio calculation confirms P3's dominance below 900 K, peaking at 99.8% at 200 K. At 2000 K, P1 and P4 dominate with ratios of 61.9% and 30.5%, respectively. In our search for a suitable method to calculate thermodynamic properties, we found that the atomization scheme at the CBS-QB3 level is suitable for S^{298K} and C_p^{298K} , while the isodesmic reaction scheme is recommended for $\Delta_f H^{298K}$ calculations. The calculated geometrical parameters, thermodynamic properties, and kinetic data align with existing/related literature for selected species, indicating the reliability of the study. These findings provide further mechanistic insights as well as reliable information for detailed kinetic modeling of silicon chemical vapor deposition (CVD) processes, which are of significant technological importance.

Key words: isobutene, SiH3, reaction mechanism, CBS-QB3, chemical vapor deposition (CVD)

INTRODUCTION

2 Silicon carbide (SiC) stands out as a semiconductor 3 due to its ability to operate under higher tempera-4 tures and currents, offering distinct advantages over 5 silicon-based materials like silicon dioxide (SiO₂) or $_{6}$ silicon nitride $(Si_{3}N_{4})^{1}$, 2 , 3 . The production of sili-7 con carbide typically involves methods such as chem-8 ical vapor deposition (CVD) or plasma-enhanced 9 chemical vapor deposition (PECVD). These meth-10 ods use silicon and carbon precursors, typically silane 11 (SiH₄) and hydrocarbons, to deposit the thin film of 12 the material through a controlled gas-phase combus-¹³ tion process⁴. During deposition, silane decomposes 14 into various reactive mono-silicon hydride radicals ¹⁵ like SiH, SiH₂, and SiH₃. Among these, silvl (SiH₃) ¹⁶ radicals are believed to have the highest contribution, 17 driving the hydrosilylation mechanism to form Si-C $_{18}$ bonds⁵,⁶. The use of olefins as precursors further enhances the hydrosilylation reaction. Their double 19 bonds significantly boost the chemical reactivity, en-20 21 abling more efficient and precise film deposition. This 22 enhancement underscores the importance of silvl rad-23 ical addition to double bond as a key mechanism in ²⁴ olefin hydrosilylation⁷. To better understand and optimize this process, it is crucial to study how the reactivity of different alkenes affects their interaction with silyl radicals. Such insights are vital for improving the efficiency and quality of SiC film production.

In 1990, Loh et al.⁸ experimentally reported the 29 rate constant for C₃H₆ + SiH₃ reaction at ambient condition (e.g. $k(C_3H_6) = (2.4\pm0.3)\times10^{-13}$ 31 cm³/molecule/s), which is at least two orders of mag-32 nitude larger than that for the C_2H_4 + SiH₃ reaction (e.g. $k(C_2H_4) < (3.0\pm3.0) \times 10^{-15} \text{ cm}^3/\text{molecule/s}$). 34 They also studied the effect of pressure variation on 35 the reactions, ranging from 2 to 9.5 Torr, and found 36 that pressure had no effect. Later, in 1991, Loh et 37 al.⁹ studied the gas-phase pseudo-first order reaction between SiH₃ and C₃H₆ at room temperature and pressure 9.5 Torr and reported that the rate constant 40 for $C_3H_6 + SiH_3$ reaction (e.g. $k(C_3H_6) = (1.5\pm0.5)$ 41 $\times 10^{-14}$ cm³/molecule/s) is lower than that of the 42 previous study conducted in 1990 (e.g. $k(C_3H_6) =$ $(2.4\pm0.3)\times10^{-13}$ cm³/molecule/s). They also found 44 that hydrogen abstraction pathways are exothermic 45 and silvl addition is also presumably energetically allowed. 47

However, Bottoni *et al.*¹⁰ conducted a study on the ⁴⁸ silyl-initiated oxidation with C₂H₄, and C₃H₆ in ⁴⁹

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1 1997. The optimized geometries of all species re-2 lated to the reaction mechanism of the two reactions 3 are calculated at MP2/6-31G* level and QCISD(T)/6-4 311G** level, respectively. The calculated energy bar-5 rier in this study has rejected the common belief that 6 alkyl substituent enhances the hydrogen abstraction 7 pathway¹¹ and suggests that alkyl substituent acti-8 vates olefin toward the silyl addition pathway in the 9 gas phase. Additionally, Clarkin et al¹² conducted thermochemistry and kinetic for C₂H₄ + SiH₃ ad-10 dition reaction using UQCISD(T) method with augcc-pVTZ and aug-cc-pVDZ basis sets. The resulting 12 activation energy and reaction enthalpy (e.g., $E_a =$ 13 3.3 kcal/mol, and $DH_{rxn} = -20.6$ kcal/mol at 298 K) 14 have pointed out the studies of Bottoni et al.¹⁰were 15 insufficient for accurately determining activation en-16 ergy. Liu et al.¹³also studied the addition mecha-17 nism for the C_3H_6 + SiH₃ reaction at the B3LYP/6-311++G(d,p) level and observed that the energy bar-19 rier of addition pathways is around 2.9 kcal/mol, 20 which is relatively good in accordance with the pre-21 vious research conducted by Bottoni et al.¹⁰. These studies have significantly advanced our comprehen-23 sion of kinetic and thermodynamics in the hydrosi-24 ²⁵ lylation reaction of alkenes (e.g., ethene⁸, ¹⁰, ¹² and propene⁸, ¹⁰, ¹³). However, the specific influence of 26 alkyl substituents on the relative contributions of silyl 27 addition and hydrogen abstraction pathways contri-28 29 butions remains unclarified. In this study, within the framework of investigating 30

the effect of alkyl substituents on the reactivity of 31 double bond in the hydrosilvlation reaction, the re-32 action mechanism and kinetic behavior for the reaction of isobutene with silyl radicals are examined to 34 see the effect of two methyl substituents at the same 35 double-bond carbon on the activity. The reaction 36 mechanism will be structured using electronic struc-37 ture calculations, calculated at the CBS-QB3 level 38 with hindered internal rotation (HIR) treatment at the 39 B3LYP/CBSB7 level. 40

41 METHODOLOGY

⁴² The electronic structure calculations were performed ⁴³ using the GAUSSIAN 09 program¹⁴. Among the ⁴⁴ various correlated methods available, the CBS-QB3 ⁴⁵ composite method was chosen for its balance of accu-⁴⁶ racy and computational efficiency¹⁵. The geometries ⁴⁷ of all stationary points involved in the reaction, in-⁴⁸ cluding reactants, products, intermediates, and tran-⁴⁹ sition states (TSs), were optimized using the B3LYP ⁵⁰ functional with the CBSB7 basis set¹⁶, ¹⁷, ¹⁸, ¹⁹, ²⁰. ⁵¹ Single-point energies at the CBS limit were obtained

through a predefined extrapolation scheme that com-52 bines multiple basis sets and incorporates empiri-53 cal corrections, specifically tailored to improve accu-54 racy for small organic system¹⁵. This method has been successfully applied to study the thermodynamics and kinetics of similar and larger oxygenated sys-57 tems. For example, it was used to investigate the de-58 composition of methyl-ester peroxyl radicals in the low-temperature oxidation of methyl butanoate²¹. In 60 the case of complex reaction pathways, the correct 61 transition state was confirmed by calculating the min-62 imum energy paths (MEP) from the transition state to 63 both the reactants and products using the intrinsic re-64 action coordinate (IRC) method²²,²³. 65

The standard heat of formation for isobutene involved 66 was calculated using the atomization energy method, 67 as described in reference 21, 24. Within the frame-68 work of classical statistical mechanics, the entropies 69 and isobaric heat capacities of the species were determined (detailed calculations can be found in the 71 supplementary material of Duong *et al.*)²⁵, ²⁶. These 72 calculations were carried out using the Multi-Species Multi-Channels (MSMC) code²⁶. The stochastic²⁷ 74 ²⁸ RRKM-ME rate model²⁹ in the MSMC code²⁶,³⁰ 75 , was used to determine the rate coefficients with a 76 number of trials of 10⁶ for the energy profile in Fig-77 ure 1. Our calculations also included corrections for 78 Eckart tunneling³¹ and the HIR treatments. 79

We employed the single exponential energy transfer 80 model with a temperature-dependent expression of $<\Delta E_{down}> = 250.0 \times (T/298)^{0.8} \text{ cm}^{-1}$ for N₂ bath 82 gas³². Lennard-Jones parameters were $\varepsilon/k = 82.0$ K 83 and = 3.74 Å for N₂ from Hippler *et al.*³³, while ε/k = 336 K and = 4.13 Å, based on carbonyl sulfide³⁴ 85 , for the reactant complex and intermediate adducts. 86 Density and sum of states were calculated using the 87 Beyer-Swinehart algorithma³⁵ combined with external/hindered rotational modes via FFT³⁶ with a density-of-states energy bin size of 1 cm $^{-1}$. The pre-90 reactive van der Waals (vdW) complex entrance chan-91 nel is barrierless. The initiation process was handled 92 using the inverse Laplace transform (ILT) approach 37 93 vielding k(E) and a temperature-independent HPL 94 rate constant $k^{\infty}(T) = 4.0 \times 10^{-10} \text{ cm}^3/\text{molecule/s as}$ suggested by Georgievskii et al. 38 for the hydroxyla-96 tion due to limited information on the vdW rate for-97 mation in the hydrosilylation. 98

RESULTS AND DISCUSSION

As observed in the reaction of isobutene with OH 100 radicals (cf. Figure 1), two distinct mechanisms 101 are identified: (*i*) direct hydrogen abstraction from 102



Figure 1: ZPE-corrected energy profile (0 K) for the isobutene + SiH₃ reaction. Units are in kcal/mol

¹ $CH_2=C(CH_3)_2$ by SiH₃ radicals and (*ii*) the addi-² tion of SiH₃ radicals to the C=C double bond of ³ $CH_2=C(CH_3)_2$ (1).

4 (i) Abstraction channels: Similar to the reaction of 5 isobutene with OH radicals, SiH3 radicals can ab- $_{6}$ stract a hydrogen atom from the -CH₃ and =CH₂ 7 moieties of $CH_2 = C(CH_3)_2$, which require overcom-8 ing barriers at TS1 (11.6 kcal/mol) and TS2 (23.3 9 kcal/mol), respectively (1). The most favorable di-¹⁰ rect H-abstraction pathway via **TS1** requires approx-11 imately 11.6 kcal/mol more energy than the addition pathway via TS3. Consequently, due to the significant difference in barrier heights between the abstraction 13 14 and addition processes, the H-abstraction channel is 15 expected to have a minimal effect, particularly at low temperatures. Subsequently, the final products, P1 16 and P2, are formed, with energies of -3.8 kcal/mol and 17 19.7 kcal/mol, respectively. The formation of P1 is in 18 agreement with Loh et al.9 that H-abstraction prod-19 uct could be exothermic. 20

21 (ii) Addition channels: The SiH₃ radical can add to
22 the C=C bond of CH₂=C(CH₃)₂, forming two dis23 tinct products, P3 and P4, which are located at -20.8
24 and -15.8 kcal/mol below the energy of the entrance

channel, respectively. These intermediates are accessed via the transition states TS3 and TS4. Notably, the transition state for SiH₃ addition to the C1 po-27 sition exhibits a lower barrier height (-0.3 kcal/mol) compared to the addition at the C2 position (4.2 29 kcal/mol) (see Figure 1). Note that the optimized ge-30 ometries for all species involved in the PES are de-31 picted in Figure S1. To summarize, P3 is the most 32 thermodynamically and kinetically favorable adduct which agrees with the idea that OH-addition is im-34 portant in the reaction of alkyl substituents with SiH3 35 (10, 12, 13). However, at high temperatures (e.g., $T \ge$ 1000 K), direct H-abstraction may become significant 37 due to the entropy effect at elevated temperatures³⁹. Therefore, a detailed kinetic analysis is necessary to 39 make more accurate predictions for this system, par-40 ticularly across a wide range of T&P conditions. 41 Figure 2 depicts our comparison between three 42 species, namely isobutene, SiH₃, and SiH₄, with available measurements/predictions (optimized isobutene 44 from Tian et al.'s work (1), SiH₃ from Yamada et al.'s work⁴⁰, and SiH₄ from Kuchitsu *et al.*'s work⁴¹) in terms of geometries, bond lengths, and angles. The 47 good agreement in geometries, bond lengths, and angles (i.e., within 1%) indicates the reliability of the



Figure 2: Structure comparison with Tian's group (1), Yamada's group (40), and Kuchitsu's group (41)

study. For more details on other species, please see
 the supplementary material.

3 Thermodynamic analyses

4 Table 1 compares thermodynamic data for isobutene, 5 calculated using the CBS-QB3 method, with pre-6 viously reported values. Two calculation schemes 7 (i.e., atomization and isodesmic reaction) were em-8 ployed. The atomization scheme at the CBS-QB3 level ⁹ shows good agreement with the literature for 298K and 10 C_p^{298K} (i.e., within 0.2 cal/mol/K), but discrepan-¹¹ cies were observed for $\triangle_f H^{298K}$. To address this, we 12 used an isodesmic reaction approach implemented in ¹³ our in-house RGA4HoF code⁴². The code gener-14 ated 3020 isodesmic reactions and estimated the average value. Detailed 3020 reactions are provided in 15 the supplementary material file. The $\triangle_f H^{298K}$ values 16 17 obtained from the isodesmic reaction scheme align well with the literature (i.e., within the reported un-18 19 certainty). In conclusion, the atomization scheme at ²⁰ the CBS-QB3 level is suitable for S^{298K} and C_p^{298K} , ²¹ while the isodesmic reaction scheme is recommended ²² for $\triangle_f H^{298K}$ calculations. Note that the comparison 23 for other species was not carried out due to the limited 24 literature data.

Kinetic analyses

Figure 3 presents the rate constant comparison with 26 the uncertainty of the ILT approach for the formation of **RC**. The uncertainty assessment is necessary due to the differences in the nature of the interactions of the 29 vdW complex in hydroxylation and hydrosilylation. 30 Importantly, we found that the choice of the HPL rate 31 has a minor effect at temperatures between 200 and 2000 K, resulting in a 1.0 to 1.7 times different total rate constant. This indicates that the assumption does 34 not change the kinetic behavior of the hydrosilylation. 35 Since there is no kinetic data available yet for this sys-36 tem, we presented the rate constants for the C_3H_6 37 + SiH₃ and C_2H_4 + SiH₃ systems. The upper limit is found to be comparable to the experiment of 39 C_3H_6 + SiH₃ by Loh *et al.* (1990)⁸ (1.7×10⁻¹³ vs. $(2.4\pm0.3)\times10^{-13}$ cm³/molecule/s), while the lower limit is quite far-fetched compared to the experi-42 ment on C_3H_6 + SiH₃ by Loh *et al.* $(1991)^{9}$ $(1.0 \times 10^{-13} \text{ vs.} (1.5 \pm 0.5) \times 10^{-14} \text{ cm}^3/\text{molecule/s})$ and $C_2H_4 + SiH_3$ by Loh *et al.* (1990)⁸ (1.0×10⁻¹³) 45 vs. $(3.0\pm3.0)\times10^{-14}$ cm³/molecule/s). However, note that due to differences in the nature of the reac-47 tions and the possibility that the experiment on C_3H_6 48 + SiH₃ by Loh et al. (1990) may have been overdetermined due to the photolysis of C₃H₆, further experiments on the isobutene + OH reaction are needed 51

Methodology	$ riangle_f H^{298K}$ (kcal/mol)	S ^{298K} (cal/mol/K)	C_p^{298K} (cal/mol/K)
Atomization scheme at CBS-QB3	-1.81	70.31	20.85
Isodesmic reaction scheme at CBS-QB3 $(CH_3)_2C=CH_2 + cyclo-pentane \rightarrow CH_3CH=CH_2$ + cyclo-hexane (The best-matched reaction among 3020 reactions found)	-3.97	-	-
Literature data	$\begin{array}{c} -4.03 \pm 0.38^{ 43} \\ -4.28 \pm 0.26^{ 44} \end{array}$	70.12 ⁴⁵	21.04 ⁴⁶





Figure 3: Rate constant comparison together with the uncertainty analysis of the ILT approach

for better understanding on the effect of the methyl
 groups on the activity.

- ³ We found that **P3** is dominant at temperatures below
- ⁴ 900 K, with a maximum branching ratio of 99.8% at ⁵ 200 K (cf Figure 4 and Table 2). At higher temper-
- 6 atures, **P1** and **P4** become dominant, with branching
- ratios reaching 61.9% and 30.5%, respectively, at 2000
- ⁸ K. This kinetic behavior agrees well with the predic-
- ⁹ tions discussed in the energy profile analysis. Note
- ¹⁰ that the decomposition of P3 might also be important
- 11 at high temperatures.
- 12 We tested the pressure effect on the isobutene +
- ¹³ SiH₃reaction (cf. Figure 5) at P = 7.6 76000 Torr,
- ¹⁴ inspired by the idea of Loh et al.⁸ (1990) that alkyl
- 15 substituents would exhibit no pressure effect in reac-
- ¹⁶ tions with SiH₃. This was confirmed in our study (cf.
- 17 Figure 5), as we also found no pressure effect on the

isobutene + SiH₃ reaction.

CONCLUSIONS

The kinetic mechanism of the reaction between 20 isobutene and SiH3 radicals was investigated theoreti-21 cally using the composite electronic structure method 22 CBS-QB3, combined with RRKM/ME rate model-23 ing. The study identifies two primary pathways: (i) 24 the addition of SiH₃to the double bond, and (ii) H-25 abstraction by SiH₃, resulting in various products. ²⁶ The addition pathway produces two major products, 27 P3 and P4, while the H-abstraction pathway generates 28 P1 + SiH₄ and P2 + SiH₄. Among these, the adduct P3 29 is determined to be the most thermodynamically and kinetically favorable intermediate (T < 900 K). How-31 ever, at very high temperatures (T > 900 K), P1 and P4 gain prominence. Pressure effect analysis (at P =

18



Figure 4: Calculated total and individual k(T, P) for the isobutene + SiH_3 \rightarrow products reaction

T (K)	RC	P1	P2	Р3	P4
200	0.1	0.1	0.1	99.8	0.1
298	0.1	0.1	0.1	99.7	0.2
300	0.1	0.1	0.1	99.4	0.4
400	0.1	0.1	0.1	99.2	0.6
500	0.1	0.1	0.1	96.8	3.0
600	0.1	0.2	0.1	92.4	7.3
700	0.1	0.5	0.1	84.0	15.4
800	0.1	2.0	0.1	71.7	26.1
900	0.1	5.6	0.1	55.0	39.3
1000	0.1	9.7	0.1	37.8	52.4
1100	0.0	18.2	0.1	25.3	56.3
1200	0.0	23.6	0.4	15.1	60.9
1300	0.0	30.7	0.7	9.6	59.0
1400	0.0	37.9	1.5	5.3	55.2
1500	0.0	44.1	2.1	3.5	50.3
1600	0.0	49.4	2.7	2.1	45.8
1700	0.0	53.5	3.8	1.4	41.2
1800	0.0	56.7	4.9	1.0	37.5
1900	0.0	59.0	6.1	0.6	34.3
2000	0.0	61.9	7.1	0.5	30.5

Table 2: Branching ratio for the isobutene + SiH $_3 \rightarrow$ products reaction.



7.6 - 76000 Torr) confirms that pressure has no significant influence on the reaction mechanism. The
barrierless formation of RC plays a minor role in the
hydrosilylation process, resulting in only a 1.0 to 1.7fold difference in the total rate constant. The branching ratio for product formation in the reaction confirms quantitatively that **P3** is dominant at temperatures below 900 K, reaching a maximum of 99.8%
at 200 K. At higher temperatures, **P1** and **P4** become
dominant, with branching ratios of 61.9% and 30.5%,
respectively, at 2000 K. Thermodynamic properties
for isobutene are obtained, revealing the atomization
scheme at the CBS-QB3 level is suitable for S^{298K} and

¹⁴ C_p^{298K} , while the isodesmic reaction scheme is rec-¹⁵ ommended for $\triangle_f H^{298K}$ calculations. The calculated ¹⁶ geometrical parameters, thermodynamic properties, ¹⁷ and kinetic data align with existing/related literature, ¹⁸ indicating the reliability of the study. These findings ¹⁹ provide a robust basis for detailed kinetic modeling of ²⁰ silicon CVD processes, which are of substantial tech-

²¹ nological importance.

22 ABBREVIATIONS

- 23 B3LYP: Becke, 3-parameter, Lee-Yang-Parr
- ²⁴ CVD: Chemical vapor deposition
- 25 CBS-QB3: Complete basis set Quadratic Becke3
- 26 HIR: Hindered internal rotation
- 27 IRC: Intrinsic reaction coordinate
- 28 ILT: Inverse Laplace transform
- ²⁹ MEP: Minimum energy paths

MSMC: Multi-Species Multi-Channels		
PECVD: Plasma-enhanced chemical vapor deposi-	31	
tion	32	
P: Products	33	
RRKM-ME: Rice-Ramsperger-Kassel-Marcus based	34	
master equation	35	
TSs: Transition states.	36	

CONFLICT OF INTERESTS

The authors declare that they have no competing interests. 39

AUTHORS' CONTRIBUTIONS

Uyen N-P. Tran: Data curation, Visualization, Inves-41 tigation, Writing - original draft. Loc T. Nguyen: 42 Data curation, Formal analysis, Investigation, Validation, Visualization, Writing – original draft. Tam V.-T. 44 Mai: Conceptualization, Data curation, Formal anal-45 ysis, Methodology, Validation, Visualization, Writing - review & editing. Khoi M. Le: Data curation, 47 Formal analysis. Lam K. Huynh: Conceptualization, 48 Funding acquisition, Methodology, Resources, Soft-49 ware, Supervision, Writing - review & editing. 50

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AVAILABILITY OF DATA AND MATERIALS

³ Data will be made available on request.

4 ETHICS APPROVAL AND CONSENT 5 TO PARTICIPATE

6 Not applicable.

7 CONSENT FOR PUBLICATION

8 Not applicable.

COMPETING INTERESTS

¹⁰ The author(s) declare that they have no competing in-11 terests.

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