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An Accurate Reaction Model for the High-Temperature Pyrolysis of Silane and Disilane

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Abstract: Small silicon hydrides such as silane and disilane are widely used to produce a number of value-added products, notably in electronics and photovoltaic industries. However, the reactivity of silicon based molecules have received much less consideration at high temperature compared to hydrocarbon compounds. The present study aims at assessing the performances of several reaction models from the literature in reproducing the important features of the high temperature pyrolysis of SiH₄ and Si₂H₆. The validation set is composed of 85 conditions and includes both time and temperature resolved profiles of Si, H, SiH, SiH₂ and SiH₄ obtained during the SiH₄ and Si₂H₆ pyrolysis within the following experimental conditions: X_{SiH_4} or $X_{Si_2H_6} = 0.2 - 1000$ ppm, $X_{H_2} = 0 - 15\%$, $X_{Ar} \approx 85 - 100\%$. The three kinetic models selected are from Mével et al., Babushok et al., and a new and unpublished mechanism of Petersen et al.'s model. The performance of each mechanism is assessed using five validation criteria accounting for the peak position and the species production. Rate of production analyses are performed on the three mechanisms to identify their similarities and differences. Mével's reaction model satisfactory reproduces most of the experimental data with, on average, a lower relative error to model the five criteria than the two other reference mechanisms.

Keywords: Kinetic modeling, Pyrolysis, Silicon hydrides

1. Introduction

Small silicon hydrides such as silane and disilane are widely used in the semiconductor industry to produce a number of value-added products. They have a large range of applications from insulating or protective layers [1] to silicon nanowires [2] for solar energy production [3] or in the manufacturing of catalysts and electronics products. Compared to hydrocarbon compounds, silicon based molecules have received much less consideration, especially at high temperature conditions. Concerning silane and disilane pyrolysis, Mick [4] and Woiki et al. [5] developed a reaction model composed of about 20 reactions. This scheme was later updated by Petersen and Crofton [6]. The recent kinetic mechanisms describing silane oxidation by Babushok et al. [7], Kondo et al. [8], Miller et al. [9], Mével et al. [10], and Javoy et al. [11] include more or less comprehensive sub-models for silane pyrolysis but do not present any specific validation for this sub-set of reaction. A number of mechanisms which include particle formation pathways have been developed to model chemical vapor deposition (CVD) processes [12]. Up to now, silane pyrolysis modeling studies

have focused on CVD applications and the validation of the gas phase reaction model was often performed indirectly using characteristic physical scales of the particle formation phenomena. As demonstrated by Petersen et al. [13] and Hall et al. [14], the pyrolysis sub-mechanism can play an important role during silane oxidation. For this reason and because silane accidental combustion is also a very serious issue for the semi-conductor industry [15, 16], it is important to improve the high temperature modeling of silane based mixtures.

The present study aims at assessing the performances of several reaction models from the literature in reproducing the important features of the high temperature pyrolysis of SiH_4 and Si_2H_6 . In the following section, the experimental validation data-set and the modeling tools are described. Then, the performance of the present reaction model are demonstrated and compared with other reaction models from the literature. Finally a rate of production (RoP) analysis is performed to identify the main reaction pathways of SiH_4 pyrolysis.

2. Methodology

2.1 Validation data-set

Experimental time and temperature resolved profiles of Si, H, SiH, SiH_2 and SiH_4 obtained during SiH_4 and Si_2H_6 pyrolysis have been collected as a validation database. These experimental data come from Roth's[4, 17–21] and Petersen's[6, 22–24] groups and have been obtained using the shock-tube technique within the following experimental conditions: $X_{\text{SiH}_4 \text{ or } \text{Si}_2\text{H}_6} = 0.2 - 1000 \text{ ppm}$, $X_{\text{H}_2} = 0 - 15 \%$, $X_{\text{Ar}} \approx 85 \% - 100 \%$, $T_5 = 1110 - 2934 \text{ K}$, $P_5 = 30 - 500 \text{ kPa}$. As presented in Table 1, all these data are divided in two subsets of data to separate silane and disilane pyrolysis conditions. The time history of the species profiles were measured using different techniques like atomic resonance absorption spectroscopy (ARAS), frequency modulation spectroscopy (FMS), and direct emission and absorption methods. Temperature resolved data are obtained using times to the maximum of normalized species profiles ($[I]/[R]$ where I and R are one intermediate species and the reactant, respectively). The overall data set is composed of 85 individual conditions that are represented in a total of 37 validation plots.

	# of exp. data	X_{SiH_4} [ppm]	$X_{\text{Si}_2\text{H}_6}$ [ppm]	X_{H_2} [%]	T [K]	P [kPa]	Species profiles	Ref.
SiH_4	54	0.2 - 1000	0	0 - 0.1	1205 - 2934	65 - 500	Si, SiH_4 , H, SiH_2 , SiH	[4, 6, 17, 18, 21, 22, 24]
Si_2H_6	31	0 - 500	0.2 - 100	0 - 15	1072 - 2185	30 - 130	Si, SiH_2	[4, 19, 20, 24]

Table 1: Summary of the experimental conditions used for the validation. The mole fraction balance corresponds to argon fraction.

2.2 Kinetic models and numerical tools

The characteristics of the kinetic mechanisms are summarized in Table 2. Mével's model [10, 11] has been developed to reproduce (i) the pyrolysis of SiH_4 and Si_2H_6 and (ii) the oxidation kinetics of SiH_4 with different oxidizers on wide range of operating conditions. PeOx is an unpublished mechanism from Petersen's group. This mechanism has been developed including hydrocarbon chemistry (up to C_6) and also sub-models for the pyrolysis and the oxidation of silane, with/without

H₂ and CH₄ addition. This mostly unvalidated model from 2007 is based primarily on GRI-Mech1.2 for the CH₄ and H₂ chemistry and the SiH₄ and Si₂H₆ kinetics from the earlier work of Petersen and coworkers. Babushok's model [7] has been developed to reproduce the ignition, flame speeds and the explosion limits of silane at low temperature conditions for safety purposes (room temperature and 100 kPa).

RoP analyses are performed using ANSYS with a closed homogeneous reactor (*CKReactor-GenericClosed*) and an adiabatic constant volume reactor (*CONV*).

2.3 Assessment of the performance

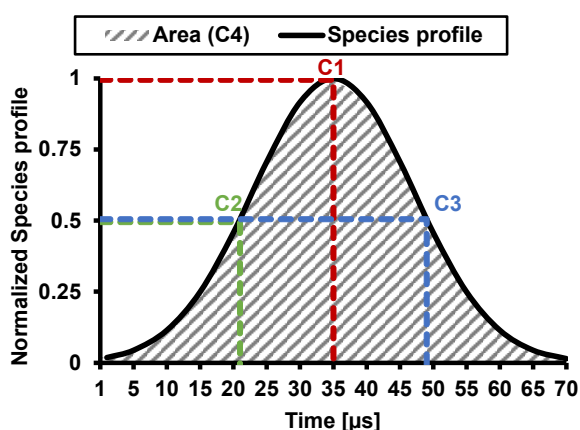
Presentation of the validation criteria The mechanisms are assessed using five validation criteria that are listed in Table 3. Figure 1 illustrates how these criteria are extracted for the two types of data available in our validation data-set. These criteria aims at accounting for both peak position or the global shape (C1, C2, C3, C5) and the quantity of the species produced (C4). It must be noted that all criteria are not extracted for all the validation profiles due to (i) the shape of the signals (e.g.: absence of C2 on a SiH₄ decaying profile) or (ii) the type of signal (e.g.: C5 is obtained from temperature resolved validation case only). Figure 2 presents an example of two criteria extracted for a given validation case.

Reaction model	Species		Reactions	
	Total	Pyro.	Total	Pyro.
Mével	92	16	448	19
PeOx	145	19	996	62
Babushok	65	20	214	55

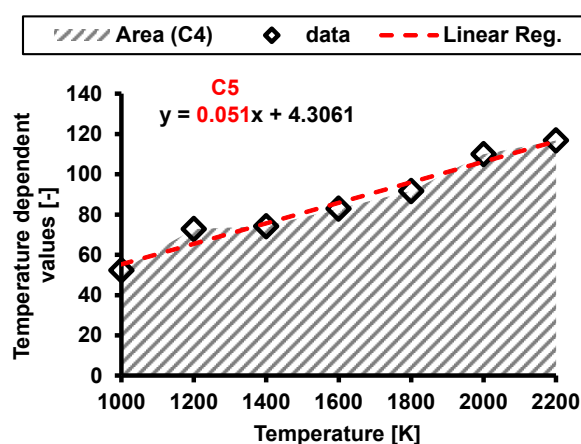
Table 2: Description of the mechanisms used. The total size of the mechanisms as well as the size of the pyrolysis sub-mechanism are indicated.

	Description	Type of profiles used
C1	100% delay	
C2	50% delay (C2<C1)	Time resolved
C3	50% delay (C3>C1)	
C4	Area integration	Time & Temp. resolved
C5	Temp. coefficient	Temp. resolved

Table 3: Validation criteria used in the present study.



a) Typical validation case



b) Two examples of criteria extracted

Figure 1: Presentation of the criteria on the two types of data available in the validation data-sets

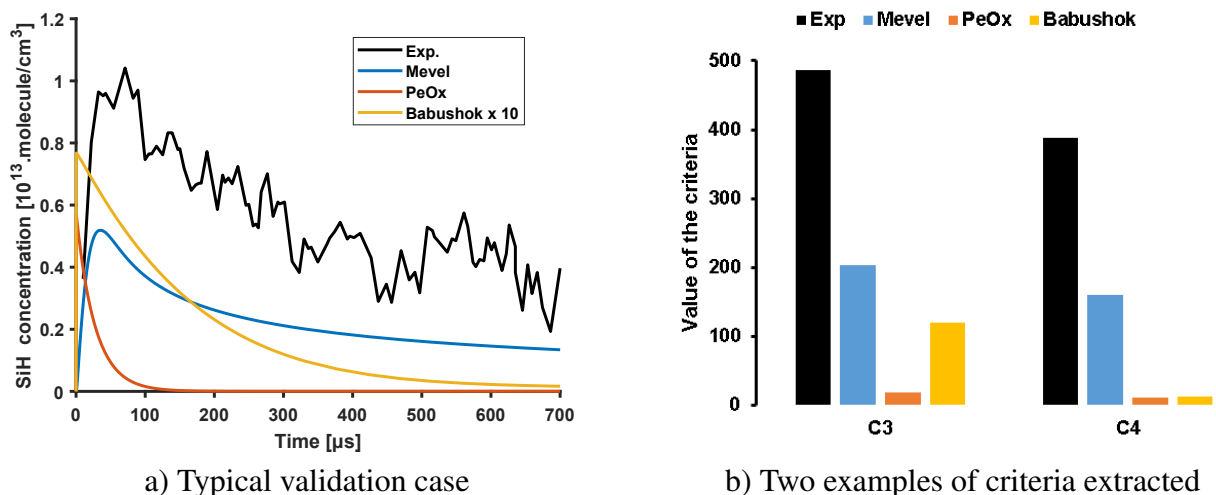


Figure 2: Illustration of the criteria used to assess the performances of the reaction models.

Analyses using the validation criteria To enable a rapid evaluation of the model performances, we perform a statistical analyses on the various criteria we have defined. For each mechanism and for each conditions (j), we calculate the relative error (RE) of each criteria (C_i), as presented in Equation 1.

$$RE_{C_i,j} = \frac{C_{i,j,mod} - C_{i,j,exp}}{C_{i,j,exp}} \quad (1)$$

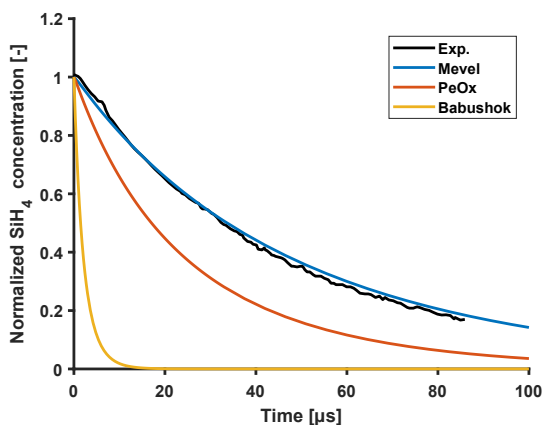
Then, the RE values are analyzed considering either the overall data-set ($j = 1$ and $k = 37$) or a subset of data specific to a given species profile, as presented in Equation 2. Such an analysis has some limitations: (i) due to the use of absolute values, the sign of the error is not maintained; (ii) the use of $RE_{C_i,avg}$ favors the mechanisms that underestimate the experimental data, since the values of $RE_{C_i,i}$ for an underestimated criteria is within the range $[-1 : 0]$ whereas these values are within the range $[0 : +\infty]$ for an overestimated one.

$$RE_{C_i,avg} = \frac{1}{k} \times \sum_j^k |RE_{C_i,j}| \quad (2)$$

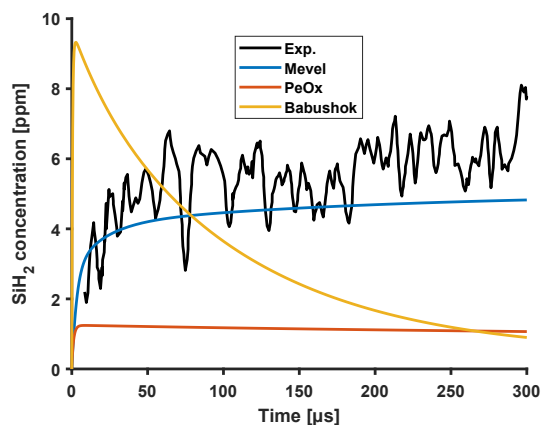
3. Results and Discussion

Figure 3 presents six validation cases that have been obtained with the three mechanisms for different species profiles with the two data-sets considered in this work. For these examples, the overall shape and the amplitude is better reproduced by Mével's model compared to the two other mechanisms. Except for c), the discrepancy between Mével's model and the experimental signals are much lower than a factor of two. The amplitude is reproduced by Mével's model within a factor of three in Figure 3 c), while the two other mechanisms underestimate the H concentration by more than one order of magnitude. In Figure 3 b), d), and e) either PeOx, Babushok or both mechanisms do not reproduce the shape of the experimental signals.

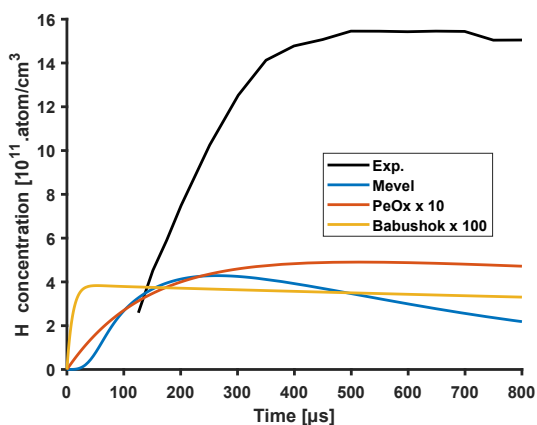
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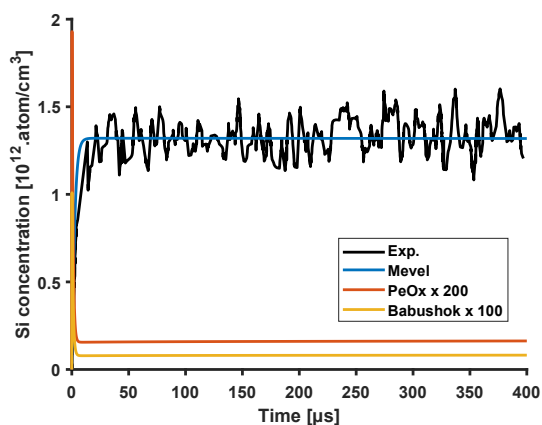
a) Conditions: $X_{\text{SiH}_4} = 1000$ ppm, $T = 1438$ K, and $P = 192.5$ kPa.



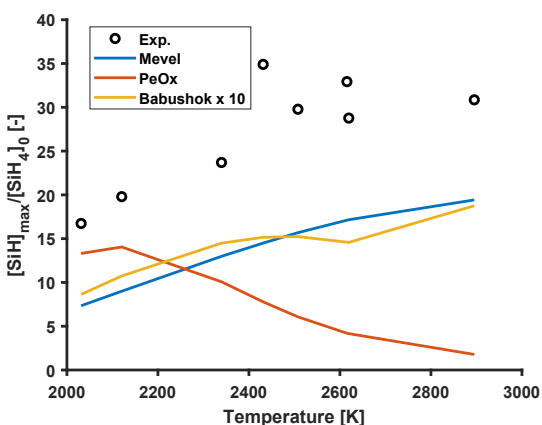
b) Conditions: $X_{\text{SiH}_4} = 1000$ ppm, $T = 1240$ K, and $P = 113.5$ kPa.



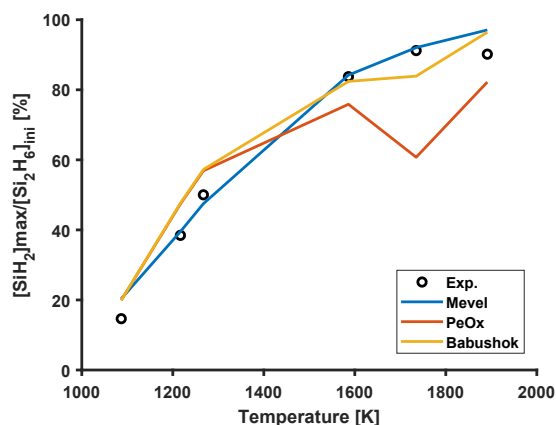
c) Conditions: $X_{\text{SiH}_4} = 5$ ppm, $T = 1336$ K, and $P = 146.9$ kPa.



d) Conditions: $X_{\text{Si}_2\text{H}_6} = 0.2$ ppm, $T = 2185$ K, and $P = 100.0$ kPa.



e) Conditions: $X_{\text{SiH}_4} = 5$ ppm, $X_{\text{H}_2} = 500$ ppm, $T = 2031$ - 2895 K, and $P = 93.0$ - 182.9 kPa.



f) Conditions: $X_{\text{SiH}_4} = 30$ ppm, $T = 1087$ - 1891 K, and $P = 30.4$ kPa.

Figure 3: Typical examples of validation cases that have been considered in the present study. The mole fraction balance is argon.

Global agreement To evaluate the overall performance of each mechanism, Equation 2 is used on the full data-set. Figure 4 presents the average |RE| for the five criteria for each mechanism. Except for C3, Mével's reaction model reproduces all criteria with a lower errors as compared to the two others mechanisms. Considering the criteria C1, C2, C4 and C5, the relative error for Mével's model is on average twice lower than the error for PeOx and between 1.5-2 times lower than the error for Babushok. This global analysis is in agreement with the typical results presented in Figure 3 and presents Mével as the most reliable reaction model out of the three tested for SiH₄ and Si₂H₆ pyrolysis.

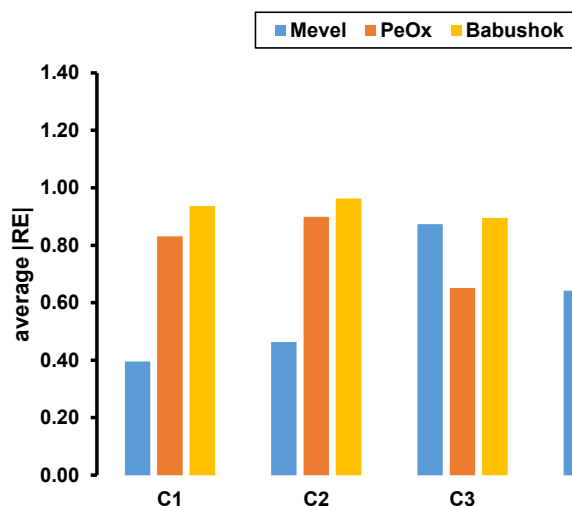


Figure 4: Average relative error to predict each criteria on all conditions.

Mechanism analyses RoP analyses are conducted for a specific condition of SiH₄ pyrolysis. Among all the reactions described in the mechanism, only the reactions contributing to more than 5% of the total RoP are considered. Then, the relative contribution of each reactions are integrated over the reaction time to get their overall contributions. Figure 5 represents these overall contributions on the production and the consumption of SiH₄, SiH₃, SiH₂, SiH, Si, H₂, H. It is noted that similar reaction pathways are observed for the three mechanisms for the production and the consumption of SiH₄ and SiH₂, while significant differences are observed for Si, H, SiH and SiH₃ species. Indeed, a common reaction pathway is identified between the three mechanisms for SiH₄ pyrolysis: SiH₄ → SiH₂+H₂; SiH₂ → Si+H₂. For both Babushok and PeOx, SiH is mainly produced through the reactions SiH₄ → SiH₃ + H; SiH₃ → SiH + H₂; H + SiH₂ → SiH + H₂, while the SiH production is driven by the reactions Si + SiH₂ → Si₂H + H; H + SiH₂ → SiH + H₂ for Mével's model.

Thus, the discrepancies between the three mechanisms seem associated to the difference in the reaction rate of Si + SiH₂ → Si₂H + H, whose the contribution is negligible for PeOx and Babushok's model.

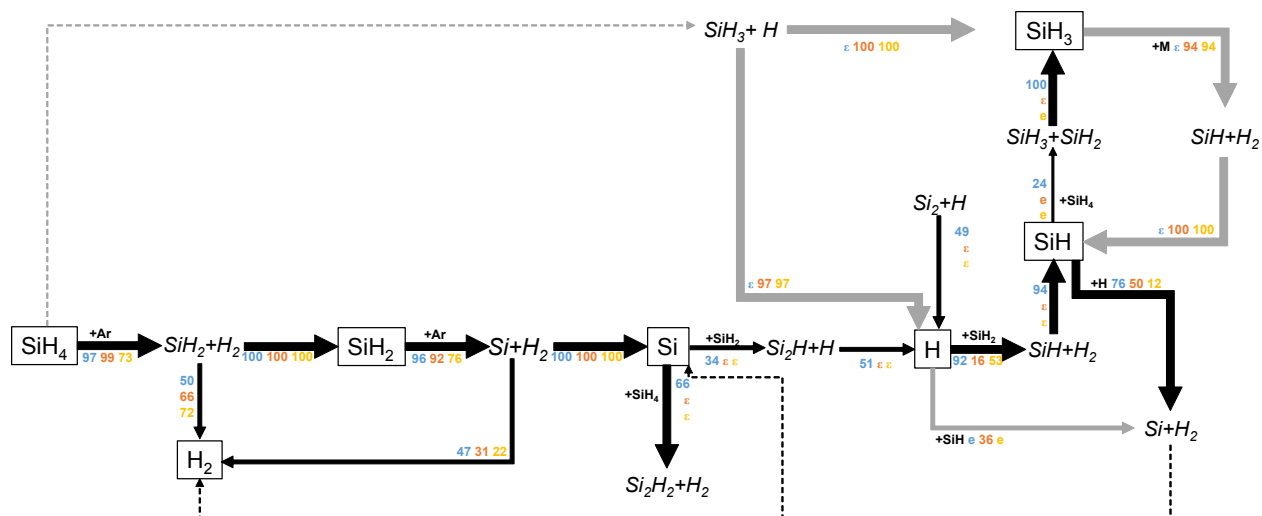


Figure 5: Flux diagram presenting the main reaction pathways for SiH_4 decomposition with the relative contribution of each reactions in each mechanism. ϵ is for reactions that are under the (5%) threshold. Conditions: $X_{\text{SiH}_4} = 0.2$ ppm (balance is Ar), $T = 1405$ K, and $P = 64.8$ kPa.

4. Conclusions

The present study aims at assessing three reference reaction models (Mével, PeOx, and Babushok) for the pyrolysis of SiH_4 and Si_2H_6 using an extensive validation data-set of 85 experimental conditions. This evaluation is performed using five validation criteria that characterize the shape and the amplitude of the experimental signals. The performance of each mechanism is assessed by calculating the mean value of the absolute relative error (average |RE|) for each criteria. Considering the full data-set, Mével’s model has the lowest RE (below 0.5 on average) for four out of five criteria. A RoP analysis allows to identify common reaction pathways between the three mechanism for SiH_4 pyrolysis: $\text{SiH}_4 \rightarrow \text{SiH}_2 + \text{H}_2$; $\text{SiH}_2 \rightarrow \text{Si} + \text{H}_2$. The discrepancies between the three mechanisms seem associated to the difference in reaction rate of $\text{Si} + \text{SiH}_2 \rightarrow \text{Si}_2\text{H} + \text{H}$, whose the contribution is negligible for PeOx and Babushok’s model.

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