

Flash pyrolysis of 1,1,2,2-tetramethyldisilane: the role of tetramethyldisilene in the

decomposition mechanism

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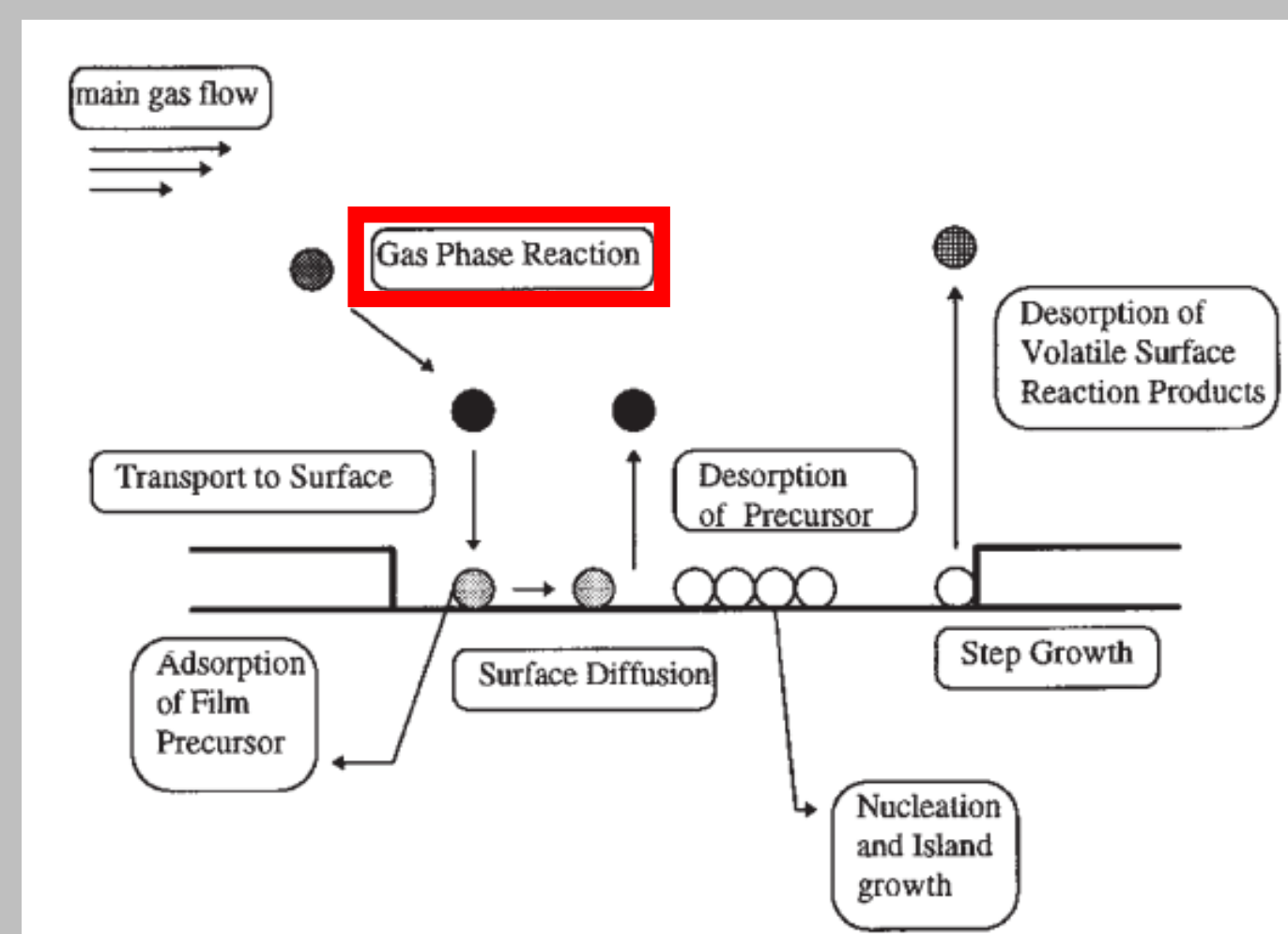
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Introduction

1. Chemical vapor deposition (CVD) of SiC film and gas phase pyrolysis of silanes.



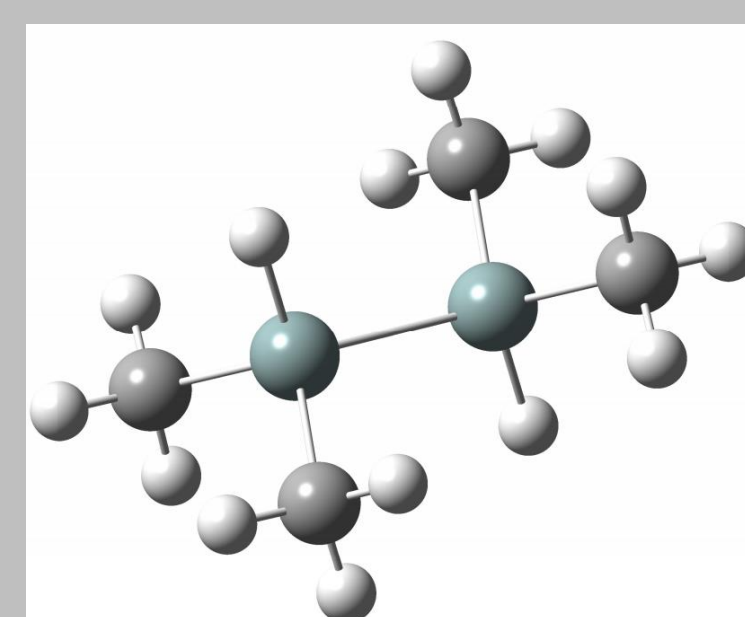
Pyrolyzing silanes was a critical step in the SiC film production using CVD. Therefore, studying its gas phase pyrolysis mechanism is important.

Jones, A. C.; Hitchman, M. L.; Royal Society of Chemistry: 2009, p. 1.

2. 1,1,2,2-tetramethyldisilane pyrolysis:

(1) is a potential precursor for the SiC thin film productions.

(2) might be a good candidate to study the sp^2 -hybridized Si by producing tetramethyldisilene ($Me_2Si=SiMe_2$) *in situ*.

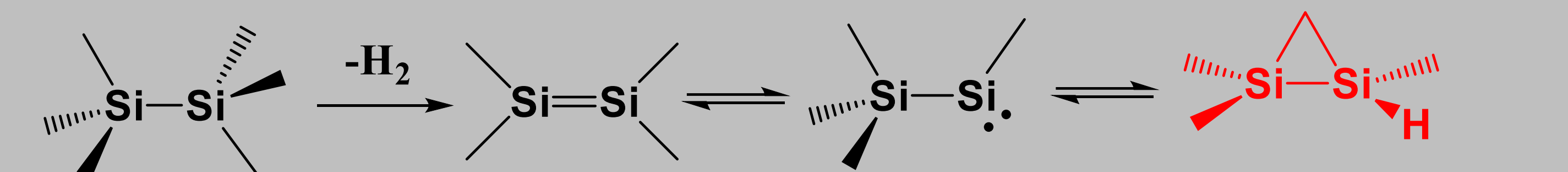
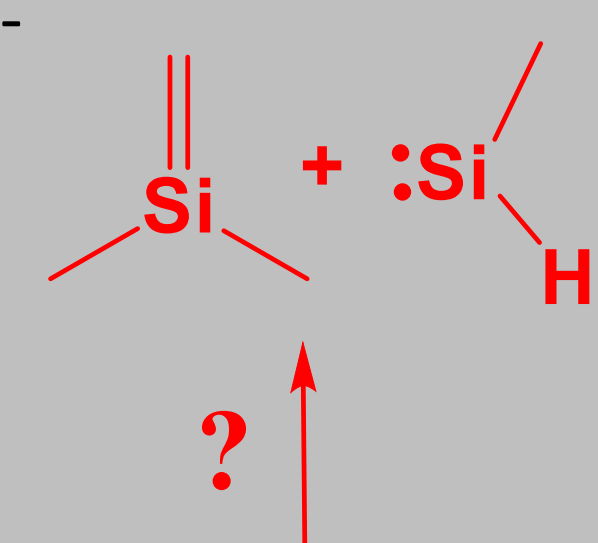


Question:

What's the role of tetramethyldisilene ($Me_2Si=SiMe_2$) in the 1,1,2,2-tetramethyldisilane pyrolysis?

Key:

Determining the existence of $Me_2Si=CH_2$ under unimolecular reaction conditions.



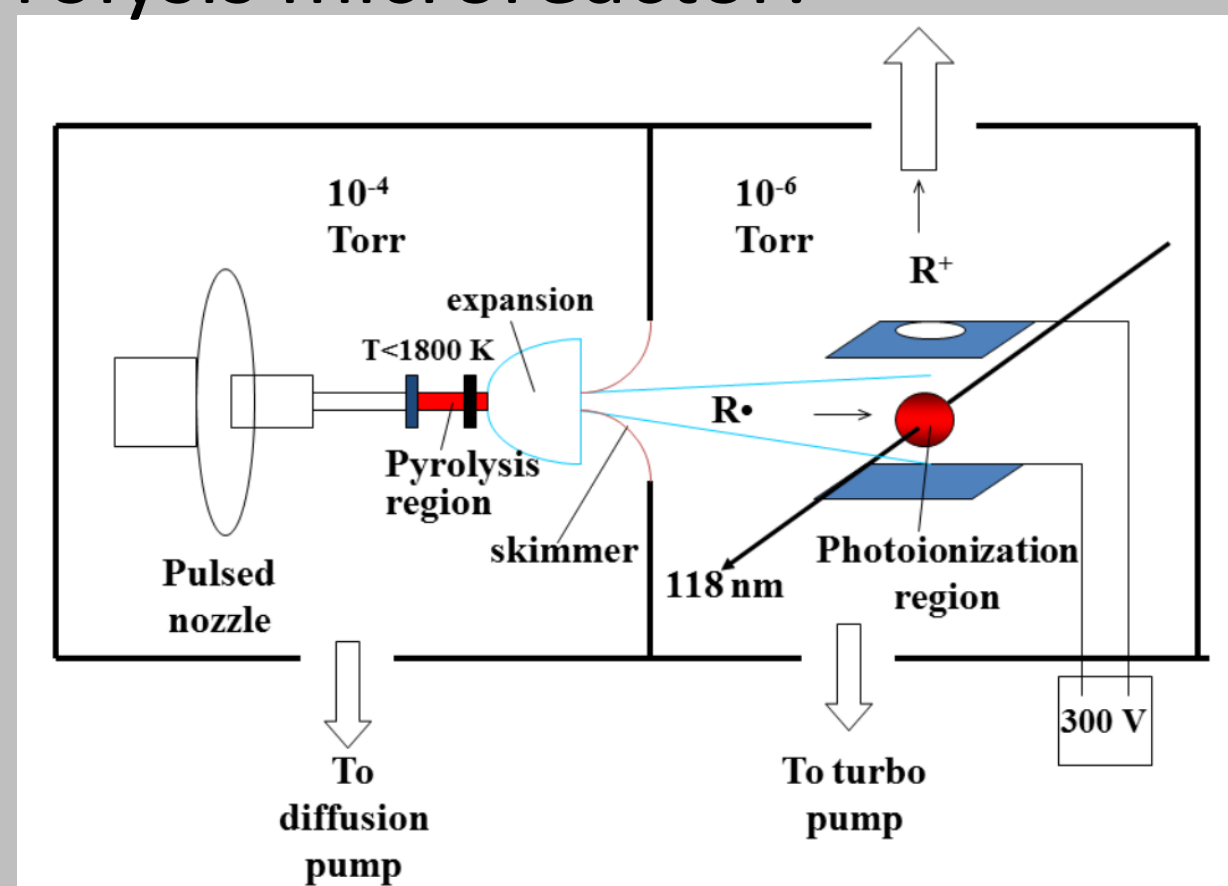
Auner, N.; Davidson, I. M. T.; Ijadi-Maghsoodi, S.; Lawrence, F. T. *Organometallics* 1986, 5 (3), 431-435
Nag, M.; Gaspar, P. P. *Chemistry - A European Journal* 2009, 15 (34), 8526-8532.

3. Approach:

- (1) Vacuum ultraviolet photoionization mass spectrometry coupled with flash pyrolysis: (**Unimolecular reactions were predominant!**)
- (2) Quantum chemistry calculations on the energetics of the decomposition pathways.

Experimental and computational method

1. Vacuum ultraviolet mass spectrometry (VUV-MS) coupled with flash pyrolysis microreactor:



Advantages:

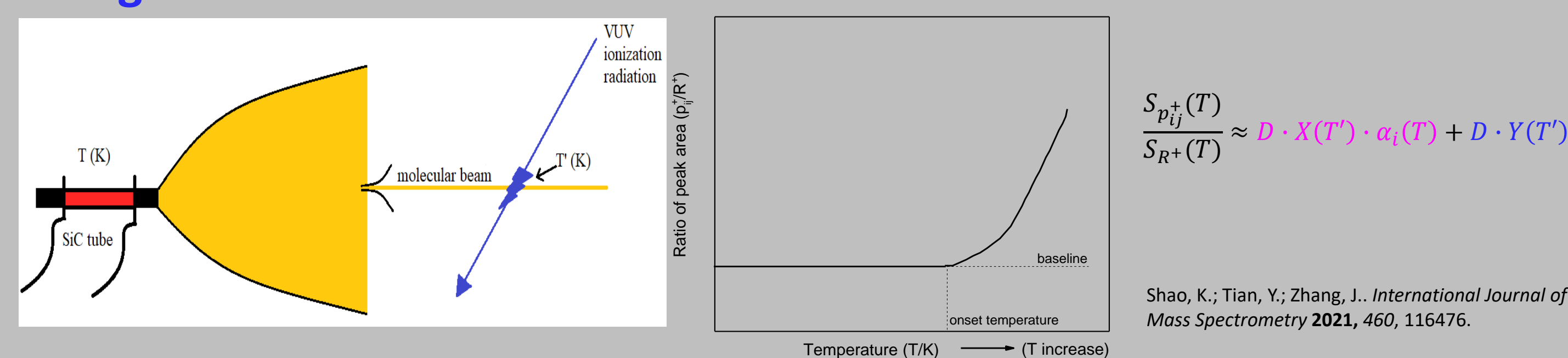
1. Mainly unimolecular reactions
2. Short reaction time (< 100 μs)
3. Detection of reactive intermediates (supersonic cooling)
4. Soft ionization (10.45 eV photon)

Jessy M. Lemieux, Ph.D Thesis University of California, Riverside 2013.

2. Reaction energetics calculations:

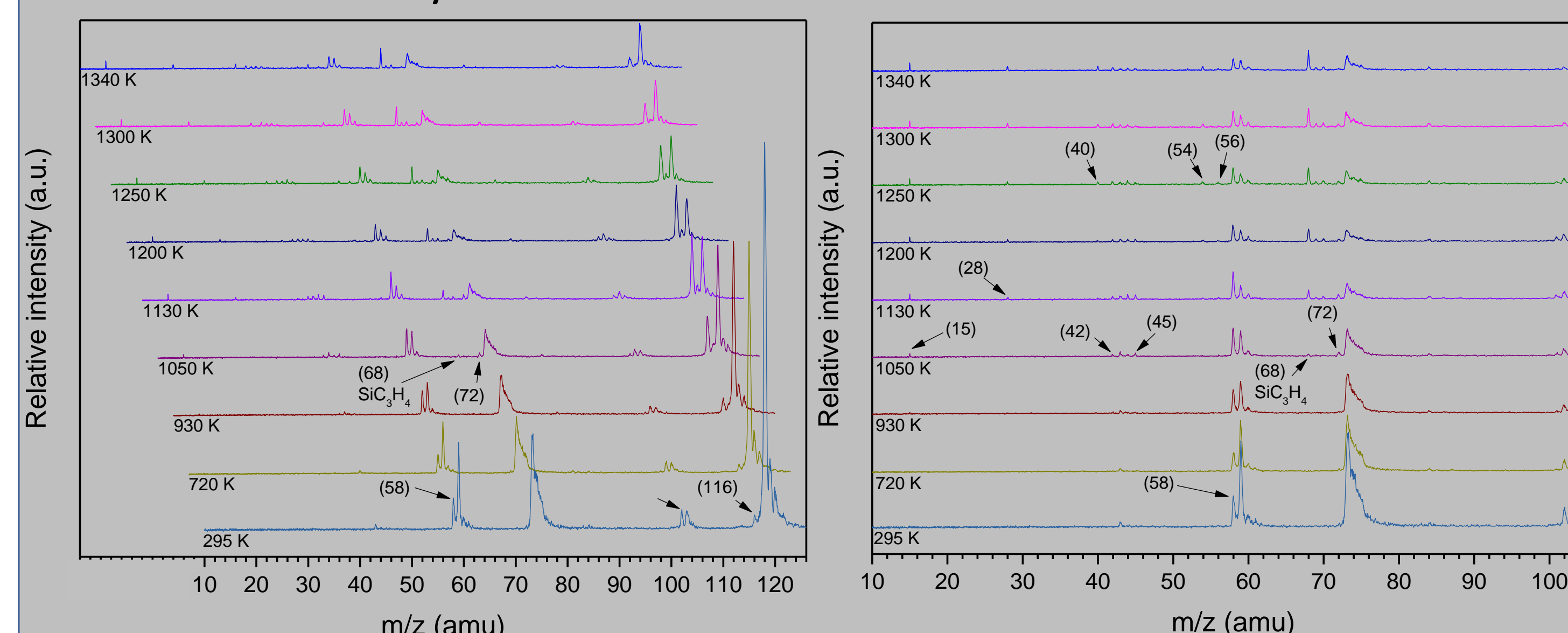
- (1) Geometry optimization and frequency calculations and single point energy calculations: UB3LYP/6-311++G(d,p).
- (2) Transition states verified using intrinsic coordinate (IRC) calculations: UB3LYP/6-311++G(d,p) level.

3. Ratio of peak area: distinguish the contributions from **ionization fragmentation** and **thermal dissociation**.

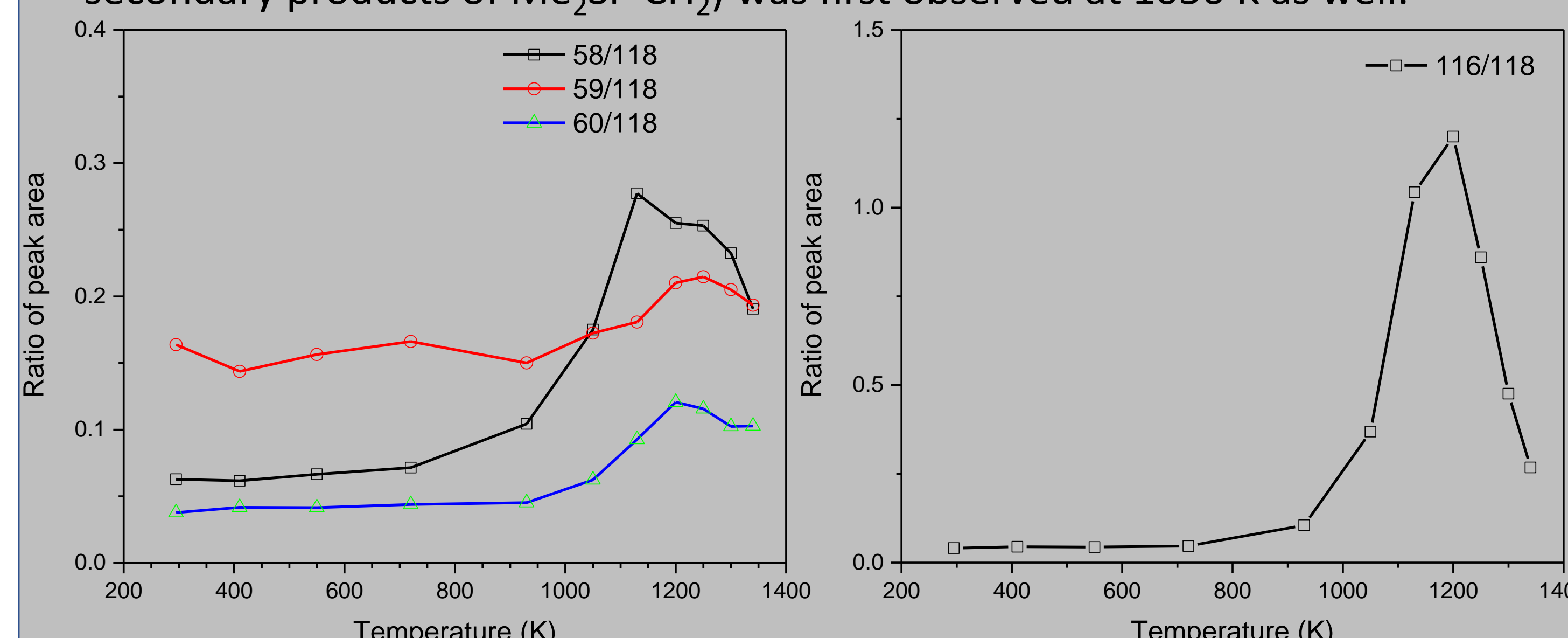


Results and Discussions

1. Main Initiation pathways in the pyrolysis of 1,1,2,2-tetramethyldisilane.

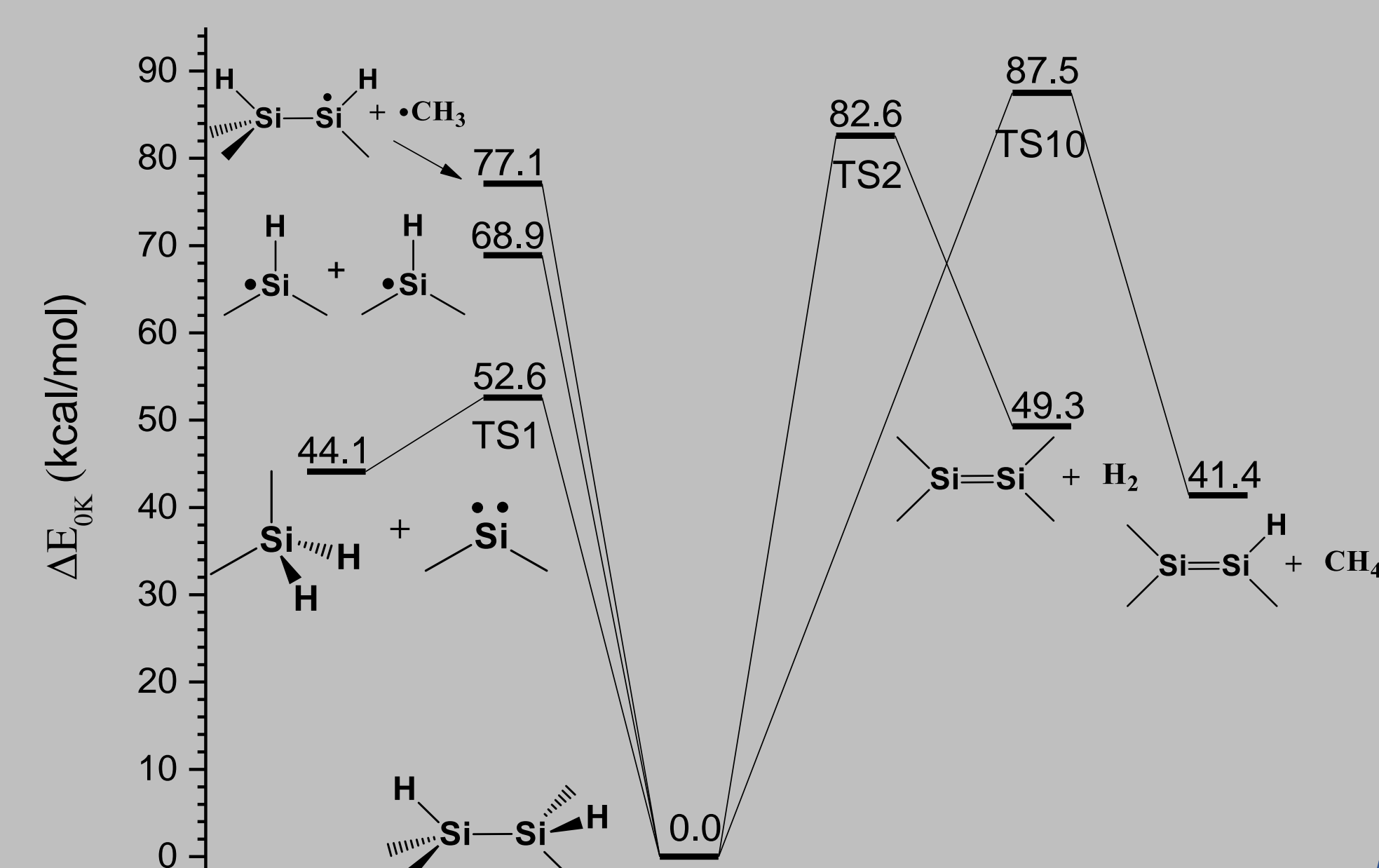


$m/z = 72$ ($Me_2Si=CH_2$) was first observed at 1050 K, and $m/z = 68$ (one of the secondary products of $Me_2Si=CH_2$) was first observed at 1050 K as well.

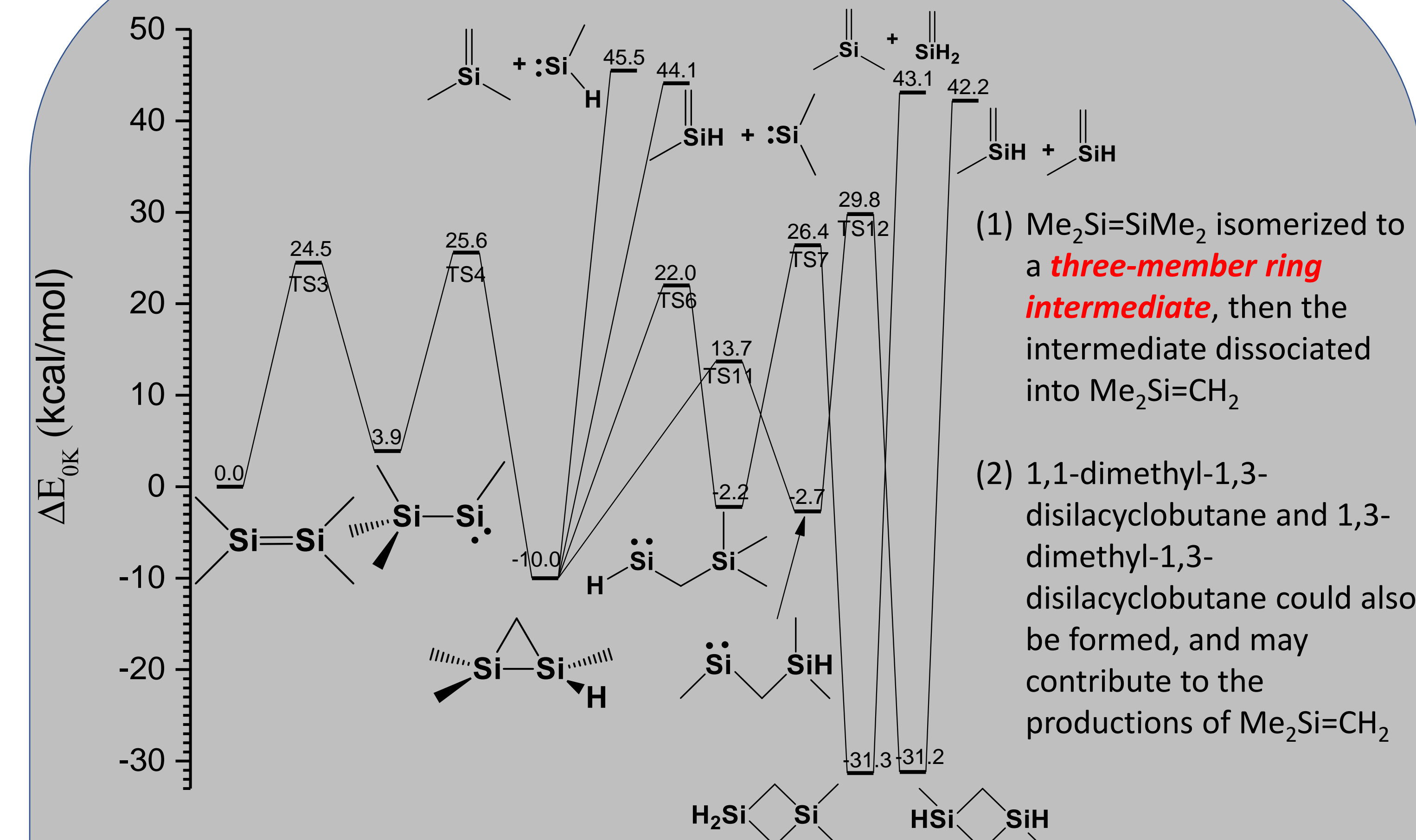


- (1) $Me_2HSi-SiHMe_2 \rightarrow Me_2SiH_2 + :SiMe_2$
- (2) $Me_2HSi-SiHMe_2 \rightarrow 2Me_2HSi\cdot$
- (3) $Me_2HSi-SiHMe_2 \rightarrow Me_2Si=SiMe_2 + H_2$

2. Quantum calculations suggest that reaction (1) and (2) are the **most energetically favorable** pathways.



3. Secondary reactions of tetramethyldisilene ($Me_2Si=SiMe_2$).



(1) $Me_2Si=SiMe_2$ isomerized to a **three-member ring intermediate**, then the intermediate dissociated into $Me_2Si=CH_2$

(2) 1,1-dimethyl-1,3-disilacyclobutane and 1,3-dimethyl-1,3-disilacyclobutane could also be formed, and may contribute to the productions of $Me_2Si=CH_2$

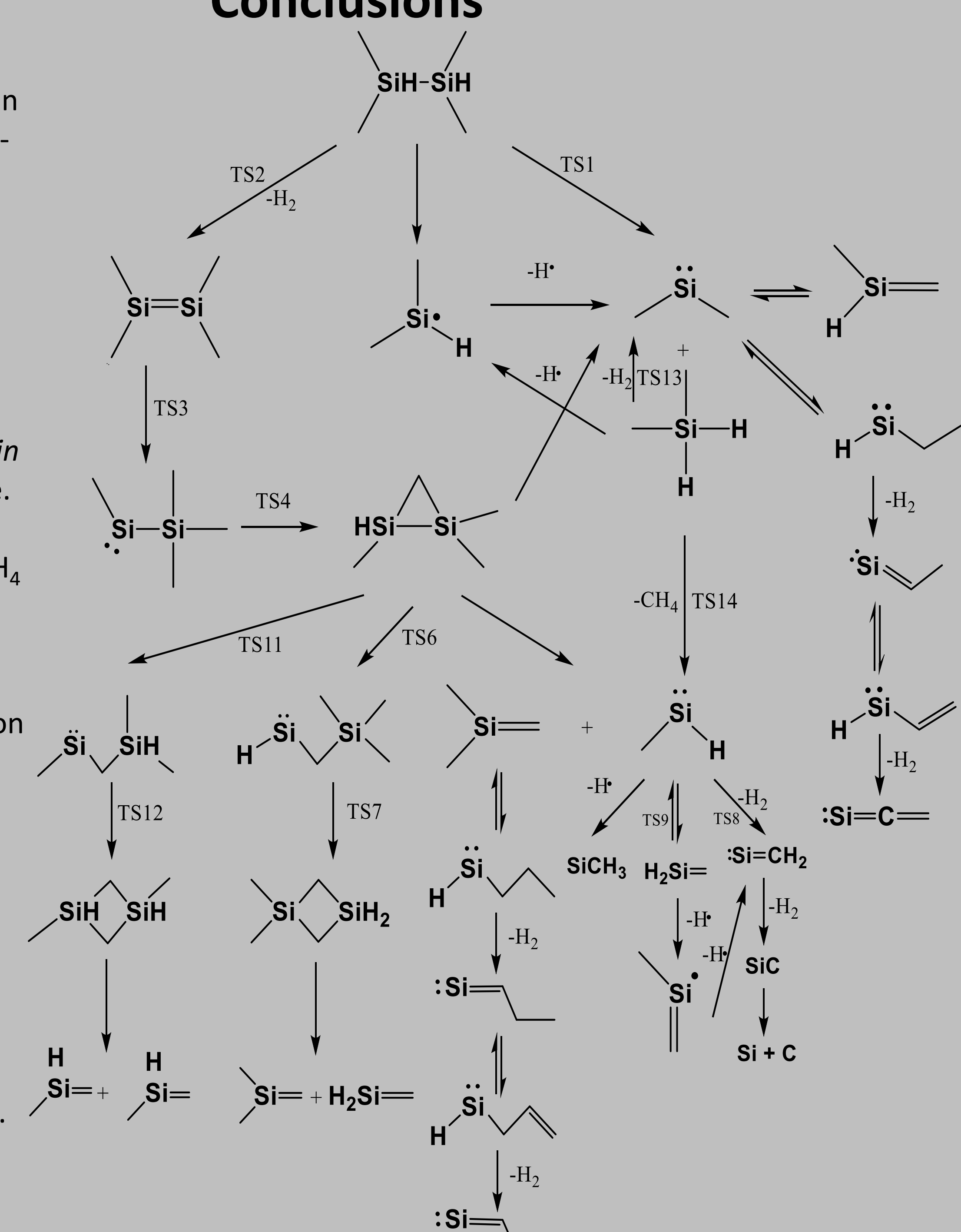
Conclusions

- (1) Three major initiation pathways for 1,1,2,2-tetramethyldisilane (reaction (1)-(3)).

- (2) Tetramethyldisilene was found to be produced in the pyrolysis of 1,1,2,2-tetramethyldisilane *in situ* for the first time. The signal of $Me_2Si=CH_2$ and SiC_3H_4 were observed as evidence.

- (3) Possible isomerization and decomposition pathways were examined theoretically.

- (4) The overall decomposition mechanism was summarized in the Scheme on the right.



Acknowledgement

