Electronic Supplementary Material for PCCP

Supplementary Information

Gas-phase kinetic and quantum chemical studies of the reactions of silylene with the methylsilanes. Absolute Rate Constants, Temperature Dependences, RRKM modelling and Potential Energy surfaces.

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Contents

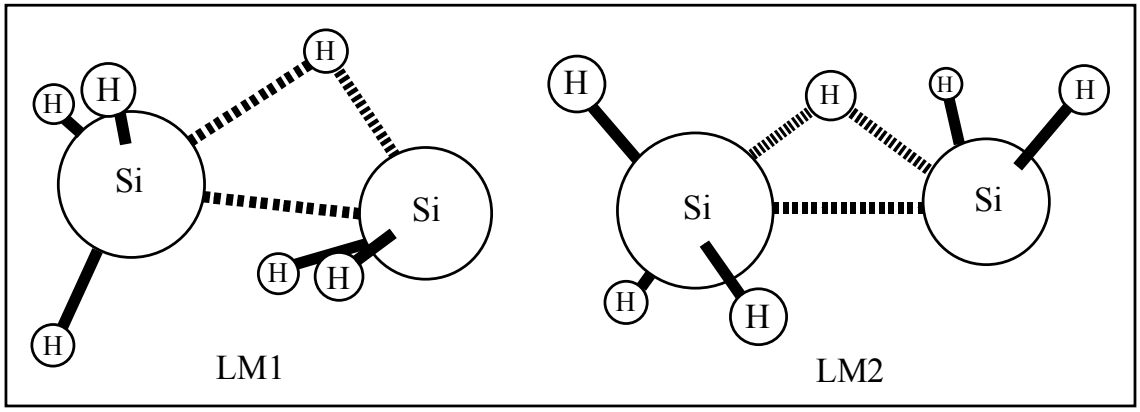


Fig. S1 Intermediate structures (local minima) found earlier in the reaction $SiH_2 + SiH_4$. (R. Becerra, H. M. Frey, B. P. Mason, R. Walsh and M. S. Gordon, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 2723).

Table S1 Molecular and transition state parameters for RRKM calculation for methyldisilane decomposition at 600 K.

	methyldisilane	methyldisilane‡
$\tilde{\nu}$ /cm^{-1}	2960(3)	2960(3)
	2165(5)	2165(4)
	1450(2)	1600(1)
	1260(1)	1450(2)
	940(2)	1260(1)
	900(1)	940(1)
	880(1)	900(1)
	850(2)	850(2)
	700(1)	700(1)
	640(1)	640(1)
	630(1)	600(1)
	590(1)	590(1)
	470(1)	585(1)
	400(1)	470(1)
	380(1)	185(1)
	185(1)	150(1)
	150(1)	120(1)
	120(1)	100(1)
		80(1)
reaction coordinate/cm^{-1}	400	
path degeneracy	3	
E_o(critical energy)/kJ mol^{-1}	204.6	
Z_{LJ}/10^{-10} cm^3 molecule^{-1} s^{-1}	5.20[a]	

[a] Value in SF_6, calculated using the formulas recommended by Troe. (J. Troe, *J. Chem. Phys.*, 1977, **66**, 4758).

Table S2 Molecular and transition state parameters for RRKM calculation for 1,1-dimethyldisilane decomposition at 600 K.

	dimethyldisilane	dimethyldisilane‡
$\tilde{\nu}$ /cm^{-1}	2960(6)	2960(6)
	2165(4)	2165(3)
	1450(4)	1600(1)
	1260(2)	1450(4)
	940(2)	1260(2)
	900(1)	940(1)
	880(1)	900(1)
	850(4)	850(4)
	700(2)	700(2)
	630(1)	615(1)
	615(1)	550(1)
	400(1)	407(1)
	380(1)	185(3)
	185(3)	150(2)
	150(2)	120(1)
	120(1)	90(1)
		80(1)
reaction coordinate/cm^{-1}	400	
path degeneracy	3	
E_o(critical energy)/kJ mol^{-1}	204.7	
Z_{LJ}/10^{-10} cm^3 molecule^{-1} s^{-1}	5.39[a]	

[a] Value in SF_6, calculated using the formulas recommended by Troe. (J. Troe, *J. Chem. Phys.*, 1977, **66**, 4758).

Table S3 Molecular and transition state parameters for RRKM calculation for 1,1,1-trimethyldisilane decomposition at 625 K.

	trimethyldisilane	trimethyldisilane‡
$\tilde{\nu}$ /cm^{-1}	2960(9)	2960(9)
	2165(3)	2165(2)
	1450(6)	1600(1)
	1260(3)	1450(6)
	940(2)	1260(3)
	880(1)	940(1)
	850(6)	850(6)
	700(3)	700(3)
	630(1)	600(1)
	400(1)	550(1)
	380(1)	185(5)
	185(5)	162(1)
	150(3)	150(3)
	120(1)	120(1)
		80(1)
reaction coordinate/cm^{-1}	400	
path degeneracy	3	
E_o(critical energy)/kJ mol^{-1}	198.9	
Z_{LJ}/10^{-10} cm^3 molecule^{-1} s^{-1}	5.85[a]	

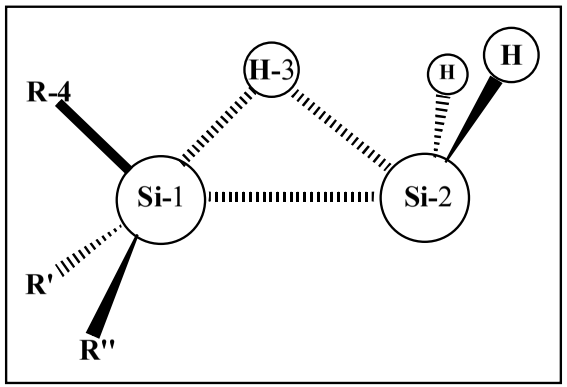
[a] Value in SF_6, calculated using the formulas recommended by Troe. (J. Troe, *J. Chem. Phys.*, 1977, **66**, 4758).

Table S4 Some Lennard-Jones parameters.[a]

Molecule	σ/Å	(ε/k)/K
SF_6	5.13	222
$MeSiH_2SiH_3$	5.30	335
$Me_2SiHSiH_3$	5.80	365
Me_3SiSiH_3	6.30	395

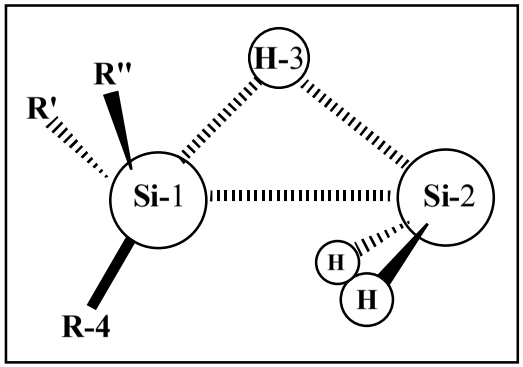
[a] Values or estimates based on data from Reid et al.
(R.C. Reid, J. M. Prausnitz and B. E. Poling, *The properties of gases and liquids*, 4th edn., McGraw-Hill, New York, 1988).

Table S5 Geometries (MP2/6-311G(d,p) level) for pathway 2. Bond lengths in Å, angles in degrees.



Reaction	LM bond 1,2	LM bond 2,3	LM angle 1,2,3	LM angle 3,1,4	TS bond 1,2	TS bond 2,3	TS angle 1,2,3	TS angle 3,1,4
$SiH_2 + SiH_4$	2.70	1.76	32.8	97.0	2.45	1.66	42.9	87.1
$SiH_2 + MeSiH_3$	2.68	1.73	33.5	94.7	2.47	1.66	42.1	86.8
$SiH_2 + Me_2SiH_2$	2.67	1.71	33.8	92.8	2.46	1.65	43.0	84.8
$SiH_2 + Me_3SiH$	2.74	1.71	31.4	95.5	2.46	1.63	44.0	85.5

Table S6 Geometries (MP2/6-311G(d,p) level) for pathway 1. Bond lengths in Å, angles in degrees.



Reaction	LM bond 1,2	LM bond 2,3	LM angle 1,2,3	LM angle 3,1,4	TS bond 1,2	TS bond 2,3	TS angle 1,2,3	TS angle 3,1,4
$SiH_2 + SiH_4$	2.47	1.53	55.9	148.6	2.49	1.5	64.2	146.4
$SiH_2 + MeSiH_3$	2.49	1.53	52.4	149.9	2.5	1.49	63.9	147.6