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ELECTRONIC SUPPLEMENTARY INFORMATION

Silane-initiated nucleation in chemically active plasmas: Validation of density functionals, mechanisms, and pressure-dependent variational transition state calculations

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Table S1. Classical forward barrier (kcal/mol) and energy of reaction for benchmark study; mean unsigned errors (MUEs, in kcal/mol) computed based on CCSD(T)/CBS reference data. Single point energies are computed based on M08-HX/MG3S geometries.

	R1		R2		R3		R4		R5		
Model chemistries	$V_f^{\ddagger}$	ΔE	$V_f^{\ddagger}$	ΔE	$V_f^{\ddagger}$	ΔE	$V_f^{\ddagger}$	ΔE	$V_f^{\ddagger}$	ΔE	MUE
M08-HX/MG3S	26.00	24.28	-4.57	-28.86	20.22	21.75	8.80	-18.69	25.81	-10.72	1.92
M08-HX/jun-cc-pVTZ	25.83	24.15	-4.73	-28.84	20.12	21.33	8.89	-18.38	25.81	-10.48	2.07
M08-HX/jul-cc-pVTZ	25.75	24.05	-4.67	-28.77	20.17	21.43	8.71	-18.52	25.95	-10.39	2.07
M08-SO/MG3S	27.23	26.48	-5.07	-29.17	22.44	23.95	10.76	-17.80	26.10	-12.76	1.02
M08-SO/jun-cc-pVTZ	26.96	26.41	-5.25	-29.25	22.44	23.86	10.63	-17.73	26.06	-12.79	1.07
M08-SO/jul-cc-pVTZ	26.84	26.30	-5.25	-29.23	22.43	23.82	10.51	-17.82	26.16	-12.69	1.08
MPW1K/MG3S	28.43	27.35	-2.99	-29.56	21.21	23.61	10.25	-17.84	27.43	-11.88	1.07
MPW1K/jun-cc-pVTZ	28.28	27.22	-3.08	-29.60	21.13	23.49	10.03	-17.86	27.36	-11.81	1.06
MPW1K/jul-cc-pVTZ	28.23	27.19	-3.10	-29.60	21.12	23.48	9.98	-17.89	27.35	-11.82	1.06
SOGGA11-X/MG3S	28.05	27.24	-2.26	-28.71	21.79	23.35	12.55	-17.31	27.46	-11.59	1.54
SOGGA11-X/jun-cc-pVTZ	27.56	26.92	-2.29	-28.78	21.83	23.25	11.97	-17.67	27.39	-11.48	1.48
SOGGA11-X/jul-cc-pVTZ	27.51	26.86	-2.29	-28.76	21.80	23.24	11.93	-17.70	27.41	-11.47	1.49
M05/MG3S	28.14	29.04	-2.55	-32.86	22.20	24.17	12.13	-19.28	23.39	-13.19	1.39
M05/jun-cc-pVTZ	27.69	28.72	-2.61	-32.96	22.06	23.78	11.96	-19.21	23.55	-12.90	1.40
CCSD(T)/CBS	28.68	27.03	-3.80	-30.92	23.64	24.52	10.04	-20.20	26.02	-12.51	0.00

Table S1. Continued

	R1		R2		R3		R4		R5		
Model chemistries	$V_f^{\ddagger}$	ΔE	$V_f^{\ddagger}$	ΔE	$V_f^{\ddagger}$	ΔE	$V_f^{\ddagger}$	ΔE	$V_f^{\ddagger}$	ΔE	MUE
M05/jul-cc-pVTZ	27.66	28.70	-2.65	-32.96	22.07	23.84	11.81	-19.29	23.48	-12.97	1.38
M05-2X/MG3S	26.59	24.87	-3.01	-30.61	22.46	24.10	10.19	-22.19	25.42	-12.35	0.98
M05-2X/jun-cc-pVTZ	26.57	24.93	-3.11	-30.57	22.37	24.10	10.06	-22.10	25.09	-12.42	0.99
M05-2X/jul-cc-pVTZ	26.47	24.83	-3.11	-30.56	22.35	24.07	9.97	-22.17	25.17	-12.34	1.02
M06/MG3S	28.65	29.50	-5.45	-28.24	22.75	25.16	11.63	-16.13	22.94	-13.17	1.78
M06/jun-cc-pVTZ	28.36	29.39	-5.53	-28.51	22.96	25.04	11.35	-16.25	22.84	-13.11	1.71
M06/jul-cc-pVTZ	28.29	29.31	-5.54	-28.52	22.91	25.01	11.28	-16.29	22.88	-13.09	1.69
M06-2X/MG3S	28.07	27.09	-3.54	-31.36	23.35	24.66	11.44	-20.32	24.21	-12.41	0.52
M06-2X/jun-cc-pVTZ	27.92	27.08	-3.59	-31.27	23.42	24.76	11.30	-20.32	23.87	-12.42	0.55
M06-2X/jul-cc-pVTZ	27.83	27.01	-3.63	-31.28	23.40	24.74	11.21	-20.38	23.94	-12.36	0.54
M11/MG3S	29.37	27.16	-3.78	-29.97	22.77	22.14	13.06	-16.83	25.70	-11.46	1.28
M11/jun-cc-pVTZ	29.01	26.95	-3.94	-29.93	22.47	21.67	12.99	-16.53	25.39	-11.47	1.38
M11/jul-cc-pVTZ	28.88	26.78	-3.86	-29.84	22.52	21.75	12.77	-16.71	25.58	-11.36	1.33
MN12-SX/MG3S	27.94	30.94	-5.31	-32.64	23.00	25.50	11.56	-18.65	24.56	-13.51	1.50
CCSD(T)/CBS	28.68	27.03	-3.80	-30.92	23.64	24.52	10.04	-20.20	26.02	-12.51	0.00

Table S1. Continued

	R1		R2		R3		R4		R5		
Model chemistries	$V_f^‡$	ΔE	$V_f^‡$	ΔE	$V_f^‡$	ΔE	$V_f^‡$	ΔE	$V_f^‡$	ΔE	MUE
MN12-SX/jun-cc-pVTZ	27.65	30.85	-5.32	-32.61	22.68	25.41	10.92	-18.70	24.64	-13.64	1.48
MN12-SX/jul-cc-pVTZ	27.59	30.76	-5.31	-32.70	22.77	25.36	10.95	-18.75	24.78	-13.50	1.44
B3LYP/MG3S	30.04	33.28	-4.87	-32.53	19.89	22.40	15.40	-15.22	27.00	-9.52	3.05
B3LYP/jun-cc-pVTZ	29.84	33.14	-5.04	-32.56	19.80	22.29	15.09	-15.24	26.93	-9.49	3.02
B3LYP/jul-cc-pVTZ	29.78	33.08	-5.05	-32.54	19.79	22.27	15.04	-15.29	26.95	-9.47	3.00
ωB97X-D/MG3S	28.80	26.71	-2.48	-28.86	21.86	22.27	12.91	-17.06	27.99	-11.07	1.73
ωB97X-D/jun-cc-pVTZ	28.59	26.58	-2.63	-28.95	21.74	22.24	12.39	-17.25	27.96	-10.97	1.66
ωB97X-D/jul-cc-pVTZ	28.53	26.54	-2.64	-28.94	21.73	22.22	12.34	-17.27	27.97	-10.97	1.67
TPSSh/MG3S	26.66	33.67	-9.14	-33.31	19.47	23.85	9.65	-16.97	24.73	-11.54	2.71
TPSSh/jun-cc-pVTZ	26.62	33.66	-9.23	-33.31	19.53	23.73	9.64	-16.80	24.71	-11.49	2.75
TPSSh/jul-cc-pVTZ	26.58	33.63	-9.25	-33.31	19.52	23.72	9.60	-16.83	24.69	-11.51	2.76
HSE06/MG3S	24.91	26.70	-4.70	-29.44	17.25	23.76	5.92	-19.54	24.91	-11.50	2.05
HSE06/jun-cc-pVTZ	24.74	26.56	-4.84	-29.47	17.15	23.66	5.64	-19.58	24.85	-11.45	2.15
HSE06/jul-cc-pVTZ	24.69	26.52	-4.85	-29.47	17.14	23.65	5.59	-19.61	24.84	-11.45	2.17
CCSD(T)/CBS	28.68	27.03	-3.80	-30.92	23.64	24.52	10.04	-20.20	26.02	-12.51	0.00

Table S1. Continued

	R1		R2		R3		R4		R5		
Model chemistries	$V_f^{\ddagger}$	ΔE	$V_f^{\ddagger}$	ΔE	$V_f^{\ddagger}$	ΔE	$V_f^{\ddagger}$	ΔE	$V_f^{\ddagger}$	ΔE	MUE
B97-3/MG3S	28.74	28.51	-1.65	-29.61	20.51	23.13	13.10	-17.58	26.79	-10.75	1.77
B97-3/jun-cc-pVTZ	28.44	28.29	-1.77	-29.75	20.36	23.08	12.54	-17.89	26.71	-10.65	1.68
B97-3/jul-cc-pVTZ	28.37	28.24	-1.77	-29.75	20.34	23.06	12.50	-17.93	26.71	-10.65	1.68
MGGA_MS2h/MG3S	26.03	28.31	-6.23	-28.74	19.71	23.03	7.24	-16.81	26.54	-11.32	2.18
MGGA_MS2h/jun-cc-pVTZ	25.88	28.18	-6.36	-28.77	19.62	22.89	6.99	-16.78	26.61	-11.19	2.27
MGGA_MS2h/jul-cc-pVTZ	25.85	28.16	-6.37	-28.77	19.62	22.89	6.97	-16.81	26.61	-11.21	2.27
PBE0/MG3S	25.07	26.48	-4.62	-29.35	17.62	23.75	5.76	-19.58	24.90	-11.68	2.02
PBE0/jun-cc-pVTZ	24.92	26.34	-4.74	-29.37	17.53	23.62	5.51	-19.59	24.85	-11.61	2.12
PBE0/jul-cc-pVTZ	24.86	26.30	-4.76	-29.37	17.51	23.61	5.47	-19.62	24.84	-11.62	2.13
tHCTHhyb/MG3S	26.97	28.69	-3.48	-29.15	17.86	23.58	9.08	-18.14	25.50	-10.47	1.78
tHCTHhyb/jun-cc-pVTZ	26.85	28.63	-3.65	-29.14	17.81	23.49	8.83	-18.08	25.44	-10.44	1.82
tHCTHhyb/jul-cc-pVTZ	26.79	28.58	-3.66	-29.15	17.79	23.47	8.78	-18.12	25.46	-10.43	1.82
MN15-L/MG3S	27.18	29.49	-5.21	-30.72	22.35	23.37	8.82	-17.74	25.82	-13.11	1.25
MN15-L/jun-cc-pVTZ	26.80	29.19	-5.35	-30.74	22.44	23.64	7.98	-18.37	25.75	-13.21	1.27
CCSD(T)/CBS	28.68	27.03	-3.80	-30.92	23.64	24.52	10.04	-20.20	26.02	-12.51	0.00

Table S1. Continued

	R1		R2		R3		R4		R5		
Model chemistries	$V_f^‡$	ΔE	$V_f^‡$	ΔE	$V_f^‡$	ΔE	$V_f^‡$	ΔE	$V_f^‡$	ΔE	MUE
MN15-L/jul-cc-pVTZ	26.45	28.91	-5.33	-30.71	22.37	23.49	7.87	-18.56	25.96	-12.95	1.25
MN12-L/MG3S	26.81	29.35	-5.82	-31.36	19.51	23.80	5.87	-18.05	24.29	-13.26	2.03
MN12-L/jun-cc-pVTZ	26.28	28.83	-5.74	-31.17	19.76	23.94	5.33	-18.58	24.29	-13.41	1.98
MN12-L/jul-cc-pVTZ	26.16	28.67	-5.68	-31.12	19.82	23.79	5.42	-18.58	24.43	-13.26	1.94
M11-L/MG3S	28.57	32.14	-5.72	-34.95	21.74	22.04	16.04	-16.81	29.24	-11.29	2.94
M11-L/jun-cc-pVTZ	27.78	32.01	-6.60	-35.11	20.67	22.98	12.65	-18.19	28.65	-12.10	2.50
M11-L/jul-cc-pVTZ	27.48	31.62	-6.43	-35.02	20.88	23.02	12.50	-18.51	28.98	-11.83	2.46
CCSD(T)/CBS	28.68	27.03	-3.80	-30.92	23.64	24.52	10.04	-20.20	26.02	-12.51	0.00

Table S2. Reaction symmetry numbers

		forward	reverse
RA	step 1	12	1
	step 2	1	2
RB	step 1	1	1
	step 2	12	1
	step 3	1	2
RC	step 1	12	6
	step 2	6	2
	step 3	1	3
RD	step 1	36	9
	step 2	9	2

Table S3. MS-T factors for activation at various temperatures for reverse reactions computed at M06-2X/MG3S level.

	RA		RB			RC			RD	
T/K	Step 1	Step 2	Step 1	Step 2	Step 3	Step 1	Step 2	Step 3	Step 1	Step 2
298	1.04	0.79	1.55	2.10	1.45	0.45	0.75	1.60	0.64	0.67
300	1.04	0.79	1.55	2.10	1.46	0.45	0.75	1.61	0.64	0.67
400	1.19	0.75	1.51	2.03	1.70	0.41	0.78	1.85	0.61	0.66
500	1.34	0.75	1.53	1.95	1.94	0.37	0.83	2.11	0.59	0.66
600	1.47	0.76	1.57	1.87	2.19	0.34	0.88	2.38	0.57	0.66
700	1.58	0.78	1.62	1.80	2.43	0.31	0.94	2.67	0.55	0.67
800	1.67	0.81	1.67	1.73	2.67	0.28	1.00	2.95	0.53	0.68
900	1.75	0.84	1.73	1.67	2.90	0.26	1.07	3.23	0.50	0.69
1000	1.83	0.87	1.79	1.61	3.13	0.25	1.13	3.52	0.48	0.70
1500	2.08	1.02	2.08	1.38	4.18	0.18	1.48	4.83	0.40	0.78

Table S4. MS-CVT/SCT rate constants for reverse reactions computed at M06-2X/MG3S level at various temperatures. For bimolecular reactions, units of rate constants are cm^3 $molecule^{-1}$ s^{-1}; for unimolecular reactions, units are s^{-1}.

	RA		RB			RC			RD	
T/K	Step 1	Step 2	Step 1	Step 2	Step 3	Step 1	Step 2	Step 3	Step 1	Step 2
298	6.85E-13	1.68E-32	4.14E-09	1.07E-12	1.16E-32	1.27E-10	1.12E-36	1.05E-13	4.20E-08	1.30E-36
300	6.99E-13	2.24E-32	5.63E-09	1.10E-12	1.57E-32	1.22E-10	1.55E-36	1.56E-13	3.92E-08	1.79E-36
400	1.60E-12	1.17E-27	6.60E-04	2.50E-12	1.15E-27	3.91E-11	3.50E-31	4.71E-07	3.84E-09	3.46E-31
500	2.99E-12	9.35E-25	7.96E-01	4.13E-12	1.17E-24	2.32E-11	7.80E-28	4.03E-03	1.13E-09	6.41E-28
600	4.85E-12	8.78E-23	9.33E+01	5.99E-12	1.30E-22	1.76E-11	1.52E-25	1.72E+00	5.54E-10	1.08E-25
700	7.12E-12	2.40E-21	2.89E+03	8.02E-12	4.00E-21	1.52E-11	7.21E-24	1.39E+02	3.58E-10	4.57E-24
800	9.78E-12	3.02E-20	3.86E+04	1.01E-11	5.57E-20	1.41E-11	1.39E-22	3.84E+03	2.70E-10	7.98E-23
900	1.28E-11	2.25E-19	2.93E+05	1.22E-11	4.49E-19	1.36E-11	1.46E-21	5.16E+04	2.26E-10	7.73E-22
1000	1.61E-11	1.16E-18	1.50E+06	1.43E-11	2.46E-18	1.35E-11	1.00E-20	4.19E+05	2.01E-10	4.93E-21
1500	3.67E-11	2.11E-16	2.16E+08	2.42E-11	5.44E-16	1.50E-11	4.59E-18	2.60E+08	1.79E-10	1.75E-18

Table S5. Fitting parameters for MS-CVT/SCT rate constants for reverse reactions computed by M06-2X/MG3S.

	RA		RB			RC			RD	
Step	Step –1	Step –2	Step –1	Step –2	Step –3	Step –1	Step –2	Step –3	Step –1	Step –2
$\Delta H^{\circ}_{\mathrm{rxn},0}$	exo	endo	endo	exo	endo	exo	endo	endo	exo	endo
molecularity	bimol	bimol	unimol	bimol	bimol	bimol	bimol	unimol	bimol	bimol
ln A	-26.2778	-36.7902	22.3166	-25.4491	-35.8803	-28.8851	-41.7243	22.6021	-28.3338	-41.6634
n	1.5793	4.4048	2.6092	0.8501	4.5664	1.7829	5.6405	3.7341	2.3699	4.9580
T_0	209.4687	95.6600	103.6372	90.7768	100.8294	42.4691	107.2797	97.1944	43.7687	102.6100
E	1.3305	17.9703	20.4886	1.1559	18.5497	-3.0972	20.1734	25.9176	-5.8223	20.1702

Explanation of table: Rate constants are fitted using the following equations:

$$k = \begin{cases} A\left(\frac{T}{300}\right)^{n} \exp\left[-\frac{E(T+T_0)}{R(T^2+T_0^2)}\right] & \text{for a reaction that is endothermic (endo) at 0 K} \\ A\left(\frac{T+T_0}{300}\right)^{n} \exp\left[-\frac{E(T+T_0)}{R(T^2+T_0^2)}\right] & \text{for a reaction that is exothermic (exo) at 0 K} \end{cases}$$

For bimolecular (bimol) reactions, the units of parameter A are cm^3 $molecule^{-1}$ s^{-1}; for unimolecular (unimol) reactions, the unit of A is s^{-1}. The parameters T_0 and E are in units of K and kcal/mol respectively, and n is unitless.

Table S6. High-pressure-limit activation energies (kcal/mol) at various temperatures computed based on MS-CVT/SCT rate constants for both forward (fwd) and reverse (rev) reactions.

	RA				RB						RC						RD			
	step 1		step 2		step 1		step 2		step 3		step 1		step 2		step 3		step 1		step 2	
T/K	fwd	rev	fwd	rev	fwd	rev	fwd	rev	fwd	rev	fwd	rev	fwd	rev	fwd	rev	fwd	rev	fwd	rev
298	25.6	1.7	-3.62	25.3	24.3	27.2	30.0	1.9	-3.22	26.0	20.6	-2.8	7.4	28.5	23.7	34.9	27.7	-5.9	3.4	28.3
300	25.7	1.7	-3.61	25.4	24.4	27.3	30.0	1.9	-3.22	26.1	20.6	-2.8	7.5	28.5	23.7	35.0	27.7	-5.9	3.4	28.3
400	27.2	2.3	-3.11	26.4	25.4	28.2	31.3	2.0	-2.81	27.3	21.8	-2.4	9.4	30.2	23.8	35.9	29.2	-5.2	5.0	29.6
500	28.0	2.7	-2.64	26.9	25.7	28.4	31.9	2.2	-2.45	27.9	22.4	-1.9	10.8	31.1	24.0	36.2	30.1	-4.5	6.3	30.3
600	28.6	3.1	-2.2	27.4	25.9	28.5	32.3	2.3	-2.1	28.4	22.7	-1.5	11.9	31.8	24.2	36.4	30.8	-3.9	7.4	30.9
700	29.2	3.4	-1.77	27.9	26.1	28.6	32.8	2.4	-1.77	28.9	23.1	-1.1	12.8	32.6	24.5	36.6	31.5	-3.4	8.4	31.5
800	29.8	3.7	-1.36	28.4	26.2	28.8	33.4	2.6	-1.46	29.5	23.4	-0.7	13.7	33.3	24.8	36.9	32.2	-2.8	9.3	32.1
900	30.4	4.0	-0.96	29.0	26.5	29.0	34.0	2.7	-1.15	30.1	23.8	-0.3	14.6	34.1	25.2	37.2	33.0	-2.3	10.2	32.8
1000	31.1	4.3	-0.57	29.6	26.7	29.2	34.6	2.9	-0.84	30.7	24.2	0.1	15.5	34.9	25.5	37.6	33.8	-1.8	11.1	33.5
1500	34.8	5.7	1.34	33.2	28.5	30.8	38.3	3.7	0.62	34.4	26.5	1.9	19.9	39.5	27.3	40.1	38.3	0.7	15.5	37.4

Table S7. MS-T reaction enthalpy ($\Delta H_{rxn}^{\circ,\text{MS-T}}$, kcal/mol) computed at M06-2X/MG3S level at various temperatures (K).

	RA		RB			RC			RD	
T/K	Step 1	Step 2	Step 1	Step 2	Step 3	Step 1	Step 2	Step 3	Step 1	Step 2
298	24.4	-29.4	-2.9	28.5	-29.7	24.0	-21.2	-11.9	33.4	-25.2
300	24.4	-29.4	-2.9	28.5	-29.7	24.0	-21.2	-11.9	33.4	-25.2
400	24.8	-29.4	-2.8	29.2	-30.0	24.0	-20.7	-12.0	33.4	-24.4
500	25.2	-29.4	-2.7	29.8	-30.4	24.1	-20.3	-12.0	33.5	-23.7
600	25.5	-29.5	-2.6	30.5	-30.9	24.1	-20.0	-12.1	33.5	-23.1
700	25.9	-29.7	-2.6	31.2	-31.4	24.2	-19.7	-12.1	33.6	-22.5
800	26.2	-29.8	-2.5	31.9	-32.0	24.2	-19.5	-12.2	33.6	-21.9
900	26.6	-30.1	-2.5	32.6	-32.6	24.2	-19.4	-12.2	33.7	-21.4
1000	26.9	-30.3	-2.4	33.3	-33.2	24.3	-19.3	-12.2	33.7	-20.9
1500	28.3	-31.6	-2.3	36.7	-36.5	24.3	-19.1	-12.3	33.8	-18.8

Table S8. MS-T reaction Gibbs free energy ($\Delta G_{rxn}^{\circ,MS\text{-}T}$, kcal/mol) computed at M06-2X/MG3S level at various temperatures (K).

	RA		RB			RC			RD	
T/K	Step 1	Step 2	Step 1	Step 2	Step 3	Step 1	Step 2	Step 3	Step 1	Step 2
298	25.7	-30.5	-2.1	29.6	-30.6	23.5	-21.0	-10.9	32.2	-24.8
300	25.8	-30.5	-2.1	29.6	-30.6	23.5	-21.0	-10.9	32.2	-24.8
400	26.2	-30.8	-1.8	29.8	-30.9	23.3	-21.1	-10.6	31.8	-24.8
500	26.5	-31.2	-1.6	30.0	-31.1	23.1	-21.2	-10.2	31.3	-24.9
600	26.7	-31.6	-1.3	30.0	-31.2	22.8	-21.4	-9.8	30.9	-25.2
700	26.8	-31.9	-1.1	29.9	-31.4	22.6	-21.7	-9.4	30.4	-25.4
800	26.9	-32.2	-0.9	29.8	-31.4	22.4	-22.0	-9.0	30.0	-25.8
900	27.0	-32.5	-0.7	29.7	-31.5	22.2	-22.3	-8.6	29.5	-26.2
1000	27.0	-32.7	-0.5	29.4	-31.5	21.9	-22.6	-8.2	29.1	-26.6
1500	26.8	-33.7	0.4	27.8	-30.9	20.8	-24.3	-6.2	26.7	-28.9

Table S9. Vibrational frequencies (in cm^{-1}) and geometric mean frequencies for $(SiH_3)_2SiHSiH^-$ and $(SiH_3)_2SiHSiH_2^-$

Mode	$(SiH_3)_2SiHSiH^-$	$(SiH_3)_2SiHSiH_2^-$
1	67.6166	58.8504
2	74.9266	66.5131
3	81.1074	82.1663
4	95.0748	91.6251
5	114.2145	112.326
6	125.9215	112.4406
7	321.9349	316.8832
8	399.5684	402.6448
9	410.5671	411.1731
10	417.2896	419.2265
11	438.9300	420.4801
12	466.7933	457.8820
13	543.322	543.5513
14	615.2602	589.0933
15	665.2141	610.4654
16	674.6209	676.7617
17	860.1783	688.0845
18	886.6351	862.2496
19	926.5675	889.5588
20	933.1321	914.7227
21	934.0968	929.7188
22	937.4362	934.9686
23	1909.0212	935.4441
24	2053.4916	939.3056
25	2114.4137	1939.9409
26	2134.0820	1945.8709
27	2148.7552	2059.359
28	2153.5027	2128.9543
29	2153.8935	2136.04
30	2159.634	2147.6447
31	–	2151.3287
32	–	2156.7592
33	–	2162.7684
Geometric mean frequencies	580.881	603.725

Table S10. The *m* parameters used in SS-QRRK calculations.

	RB step 1		RC step 3	
T/K	E_a/(kcal mol^{-1})	*m*	E_a/(kcal mol^{-1})	*m*
298	24.3	14.6	23.7	13.7
300	24.4	14.7	23.7	13.7
400	25.4	15.3	23.8	13.7
500	25.7	15.5	24.0	13.9
600	25.9	15.6	24.2	14.0
700	26.1	15.7	24.5	14.2
800	26.2	15.8	24.8	14.4
900	26.5	16.0	25.2	14.5
1000	26.7	16.1	25.5	14.7
1500	28.5	17.2	27.3	15.8

Table S11. Numbers of distinguishable conformers found in the conformational searches for the species that have multiple structures

Molecule	Number	Molecule	Number
$SiH_3SiHSiH_2^-$	4	RC Step 1 TS	2
$(SiH_3)_2SiHSiH_2^-$	4	$(SiH_3)_2SiHSiH_2^-$	3
RA Step1 TS	6	RC Step 2 TS	2
$(SiH_3)_2SiHSiH^-$	3	RC Step 3 TS	2
RA Step 2 TS	2	RD Step 1 TS	2
$(SiH_3)_2SiH_2Si^-$	3	RD Step 2 TS	2
RB Step 1 TS	2		
RB Step 2 TS	4		
RB Step 3 TS	2		

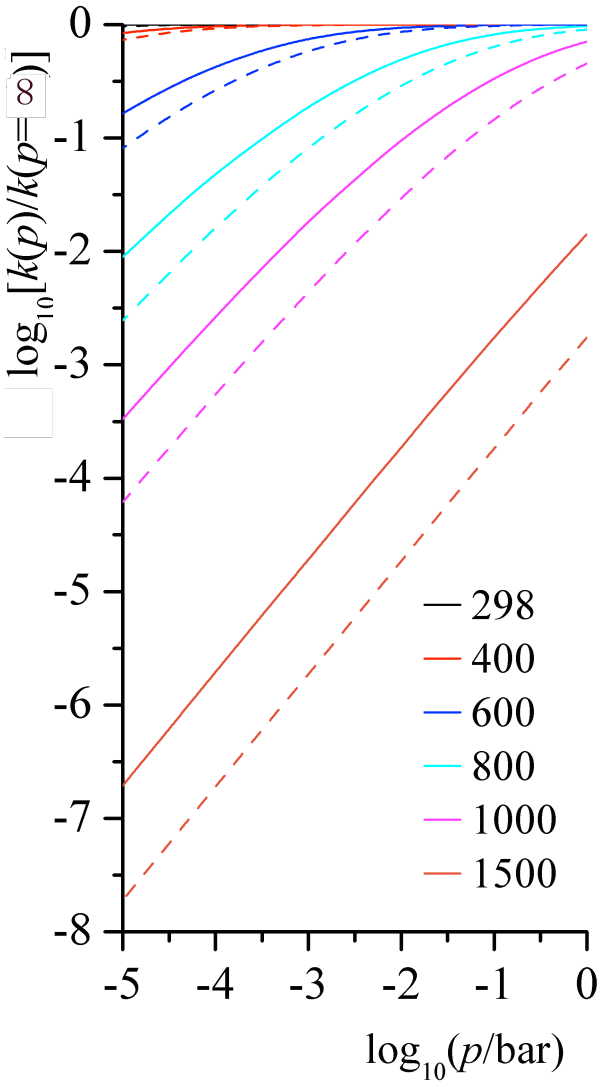

Figure S1. Predicted falloff curves for thermal rate constants of unimolecular isomerization reactions at various temperatures (K) and pressures (bar). Solid lines are for reaction RB step 1; dashed lines are for reaction RC step 3. The $\langle \Delta E \rangle$ is chosen to be 740 cal/mol.

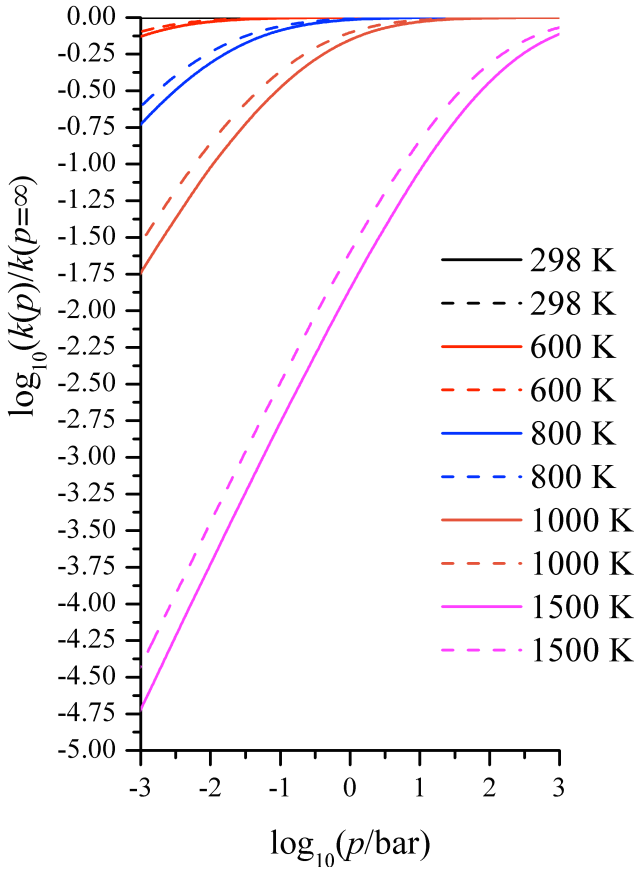

Figure S2. Predicted falloff curves for thermal rate constants of unimolecular isomerization reactions of reaction RB step 1. Solid lines are computed with $\langle \Delta E \rangle$ being 740 cal/mol; dashed lines are computed with $\langle \Delta E \rangle$ being 1480 cal/mol.