SUPPORTING INFORMATION

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Nanodusty plasma chemistry: A mechanistic and variational transition state theory study of the initial steps of silyl anion–silane and silylene anion–silane polymerization reactions

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Table S1. Cartesian coordinates (in Å) of M08-HX/MG3S optimized geometries

$Si_2H_4^-$

H	-1.723250	-1.350279	-0.000001
H	-1.711773	0.687084	1.173834
H	1.369732	1.439219	0.000002
Si	-1.042685	0.000778	0.000001
Si	1.312476	-0.105286	-0.000001
H	-1.711776	0.687088	-1.173828

$SiH_2SiHSiH_3^-$

Si	-1.751314	-0.399301	0.032261
H	-1.728688	-1.485345	-1.008044
H	-1.962009	-1.132294	1.329767
H	-3.075682	0.284656	-0.197648
Si	0.088122	1.049202	-0.173586
H	0.021440	1.652786	1.226675
Si	1.780429	-0.518139	0.110306
H	1.967936	-1.312551	-1.166077
H	3.135688	0.148076	0.249591

$SiH_3SiHSiH_3^-$

Si	-1.689110	-0.453363	0.005056
H	-1.862093	-1.217616	-1.283515
H	-1.583041	-1.547673	1.040217
H	-3.065612	0.115101	0.249910
Si	0.000001	1.186208	-0.111918
Si	1.689110	-0.453363	0.005056
H	1.583058	-1.547652	1.040240
H	1.862059	-1.217642	-1.283505
H	3.065621	0.115099	0.249868
H	-0.000001	1.387634	1.412072

SiH_4

Si	0.000000	0.000000	0.000000
H	0.858197	0.858197	0.858197
H	-0.858197	-0.858197	0.858197
H	-0.858197	0.858197	-0.858197
H	0.858197	-0.858197	-0.858197

$SiHSiH_2SiH_3^-$

H	3.125900	0.399843	0.068414
H	1.938892	-1.389269	1.094426
H	1.994077	-1.196396	-1.284130
H	0.072295	1.716656	1.255652
H	0.062022	1.831513	-1.093631
H	-1.663891	-1.152036	1.214990
Si	1.849756	-0.396050	-0.024634
Si	-0.148467	0.847613	0.034914
Si	-2.096238	-0.466586	-0.099975

TS1

Si	-1.731357	-0.540934	0.004240
Si	-0.161022	1.218123	-0.105640
Si	1.693931	-0.310761	-0.009505
H	-1.870398	-1.294382	-1.293725
H	-1.527639	-1.635124	1.022385
H	-3.136674	-0.066692	0.279359
H	-0.181579	1.406307	1.420232
H	1.505698	-1.304324	1.104157
H	1.777995	-1.028559	-1.325023
H	2.953654	0.473710	0.217514
H	3.257210	-1.680940	0.127786

TS2

Si	1.713799	-0.524511	-0.033545
Si	0.124756	1.191669	0.262180
Si	-1.655497	-0.280611	-0.203267
H	1.797778	-1.466638	1.139596
H	1.573779	-1.452026	-1.215311
H	3.125797	-0.009225	-0.161965
H	0.197903	1.590233	-1.222256
H	-1.526174	-1.308132	-1.302115
H	-2.955275	0.411935	-0.529004
H	-2.073031	-1.165550	1.006654
H	-2.703594	-2.012256	1.929253

TS3

H	1.876170	-1.774903	-0.308040
H	2.977263	0.230106	-0.978711
H	2.723542	-0.254047	1.320448
H	-0.707302	0.109641	1.197029
H	0.131373	2.121518	0.412659
H	-1.507134	-1.647990	-0.149370
Si	1.983517	-0.314827	0.010760
Si	-0.095703	0.726432	-0.117257
Si	-2.280237	-0.324771	-0.000218

$Si_2H_5^-$

H	-0.788069	1.695701	1.177016
H	1.240387	1.867157	0.000000
H	-0.788069	1.695701	-1.177016
H	0.982913	-1.341825	-1.132773
H	0.982913	-1.341825	1.132773
Si	-0.058217	1.089214	0.000000
Si	-0.058217	-1.273136	0.000000

Si_2H_6

Si	0.000000	0.000000	1.171823
H	0.000000	1.396933	1.687657
H	-1.209779	-0.698466	1.687657
Si	0.000000	0.000000	-1.171823
H	0.000000	-1.396933	-1.687657
H	-1.209779	0.698467	-1.687657
H	1.209779	0.698466	-1.687657
H	1.209779	-0.698467	1.687657

$SiH_2SiH_2SiH_3^-$

Si	1.901890	-0.393067	0.000013
H	2.010416	-1.292217	1.194288
H	2.010405	-1.292299	-1.194201
H	3.184836	0.397572	-0.000020
Si	-0.092325	0.852226	-0.000021
H	0.101418	1.779701	-1.176988
Si	-2.111456	-0.374024	0.000003
H	-1.590987	-1.282249	-1.129125
H	-1.591013	-1.282164	1.129212
H	0.101411	1.779760	1.176900

SiH_3^-

Si	0.000000	0.000000	0.144077
H	0.000000	1.311984	-0.672358
H	1.136211	-0.655992	-0.672358
H	-1.136211	-0.655992	-0.672358

$SiH_3SiHSiH_3^-$

Si	-1.689110	-0.453363	0.005056
H	-1.862093	-1.217616	-1.283515
H	-1.583041	-1.547673	1.040217
H	-3.065612	0.115101	0.249910
Si	0.000001	1.186208	-0.111918
Si	1.689110	-0.453363	0.005056
H	1.583058	-1.547652	1.040240
H	1.862059	-1.217642	-1.283505
H	3.065621	0.115099	0.249868
H	-0.000001	1.387634	1.412072

TS1

H	2.726603	-1.367525	-1.176381
H	3.868353	0.364270	-0.023603
H	2.747651	-1.331726	1.200434
H	0.742330	1.653733	1.165430
H	0.727508	1.635050	-1.179315
H	-3.360841	-0.971640	-1.281597
H	-4.319347	0.595386	0.169184
H	-3.288711	-1.323007	1.026107
H	-1.158487	0.204213	0.024232
Si	2.597728	-0.443391	-0.000431
Si	0.541376	0.705605	0.001662
Si	-3.045179	-0.223554	0.004163

TS2

H	1.512547	-1.560968	-1.001910
H	2.777796	0.371354	-0.893154
H	2.693531	-0.712254	1.106445
H	0.028875	1.859288	1.320673
H	-0.089037	2.092340	-1.042856
H	-0.539732	-1.573619	0.413520
H	-2.717005	-0.204558	-1.214338
H	-2.673677	-0.420528	1.146752
H	0.428008	-1.410703	0.955344
Si	1.760063	-0.424845	-0.044172
Si	-0.078962	1.061011	0.052320
Si	-1.782623	-0.524763	-0.064610

TS3

H	1.736977	-1.246300	-1.324311
H	3.021055	-0.078274	0.316913
H	1.363706	-1.623311	0.997540
H	-1.368210	0.559344	0.995985
H	0.344901	1.686979	1.333829
H	-1.811452	-1.603921	0.976135
Si	1.614521	-0.532824	-0.008488
Si	0.064653	1.235887	-0.116745
Si	-1.691418	-0.534920	-0.093080
H	-3.115558	-0.048503	-0.239715

Table S2. Thermodynamic and quasithermodynamic functions (in the units of kcal/mol) at various temperatures for reaction R1. Enthalpy, Gibbs free energy, and thermodynamic energy are reported with respect to reactants (SiH_4 + $Si_2H_4^-$)

T/	TS1			IN1			TS2			IN2			TS3			IN3		
K	ΔG_T°	ΔU_T°	ΔH_T°	ΔG_T°	ΔU_T°	ΔH_T°	ΔG_T°	ΔU_T°	ΔH_T°	ΔG_T°	ΔU_T°	ΔH_T°	ΔG_T°	ΔU_T°	ΔH_T°	ΔG_T°	ΔU_T°	ΔH_T°
0	19.0	19.0	19.0	16.6	16.6	16.6	17.6	17.6	17.6	-3.7	-3.7	-3.7	18.3	18.3	18.3	-5.0	-5.0	-5.0
298	27.0	19.4	18.8	19.1	17.3	17.3	25.2	18.1	17.6	-2.1	-2.5	-2.5	19.9	19.1	19.1	-3.5	-3.8	-3.8
300	27.1	19.4	18.8	19.1	17.3	17.3	25.2	18.2	17.6	-2.1	-2.5	-2.5	19.9	19.1	19.1	-3.6	-3.8	-3.8
400	29.8	19.9	19.1	19.6	17.7	17.7	27.7	18.8	18.0	-2.1	-1.9	-1.9	20.0	19.5	19.5	-3.6	-3.2	-3.2
500	32.4	20.5	19.5	20.0	18.2	18.2	30.1	19.5	18.5	-2.2	-1.3	-1.3	20.1	19.9	19.9	-3.7	-2.7	-2.7
600	34.9	21.1	19.9	20.3	18.7	18.7	32.3	20.2	19.1	-2.4	-0.9	-0.9	20.1	20.2	20.2	-4.0	-2.2	-2.2
700	37.4	21.6	20.2	20.5	19.1	19.1	34.5	20.9	19.5	-2.7	-0.5	-0.5	20.1	20.4	20.4	-4.3	-1.8	-1.8
800	39.8	22.1	20.5	20.7	19.5	19.5	36.6	21.6	20.0	-3.0	-0.1	-0.1	20.1	20.5	20.5	-4.7	-1.4	-1.4
900	42.2	22.6	20.8	20.8	19.9	19.9	38.7	22.3	20.5	-3.4	0.2	0.2	20.0	20.6	20.6	-5.1	-1.1	-1.1
1000	44.6	23.1	21.1	20.9	20.3	20.3	40.7	22.9	20.9	-3.8	0.4	0.4	19.9	20.7	20.7	-5.6	-0.8	-0.8
1500	56.0	25.2	22.2	20.9	21.9	21.9	50.1	25.7	22.7	-6.2	1.3	1.3	19.5	20.6	20.6	-8.1	0.0	0.0

Table S3. Thermodynamic and quasithermodynamic functions (in the units of kcal/mol) at various temperatures for reaction R2. Enthalpy, Gibbs free energy and thermodynamic energy are reported with respect to reactants (SiH_4 + $Si_2H_5^-$).

T/	TS1			IN1			TS2			IN2			TS3			IN3		
K	ΔG_T°	ΔU_T°	ΔH_T°	ΔG_T°	ΔU_T°	ΔH_T°	ΔG_T°	ΔU_T°	ΔH_T°	ΔG_T°	ΔU_T°	ΔH_T°	ΔG_T°	ΔU_T°	ΔH_T°	ΔG_T°	ΔU_T°	ΔH_T°
0	12.8	12.8	12.8	11.4	11.4	11.4	24.2	24.2	24.2	-5.1	-5.1	-5.1	22.5	22.5	22.5	-10.0	-10.0	-10.0
298	19.5	13.1	12.5	11.0	11.5	11.5	34.0	23.7	23.1	-3.8	-3.7	-3.7	24.6	23.3	23.3	-8.4	-8.9	-8.9
300	19.6	13.1	12.5	11.0	11.5	11.5	34.0	23.7	23.1	-3.9	-3.7	-3.7	24.6	23.3	23.3	-8.4	-8.9	-8.9
400	21.9	13.5	12.7	10.8	11.5	11.5	37.6	24.1	23.3	-4.0	-3.1	-3.1	25.0	23.7	23.7	-8.3	-8.5	-8.5
500	24.2	13.8	12.8	10.6	11.5	11.5	41.2	24.7	23.7	-4.3	-2.6	-2.6	25.2	24.2	24.2	-8.3	-8.1	-8.1
600	26.5	14.2	13.0	10.4	11.5	11.5	44.7	25.2	24.0	-4.7	-2.2	-2.2	25.4	24.5	24.5	-8.4	-7.8	-7.8
700	28.7	14.5	13.1	10.3	11.5	11.5	48.0	25.9	24.5	-5.1	-1.9	-1.9	25.6	24.8	24.8	-8.5	-7.5	-7.5
800	30.9	14.9	13.3	10.1	11.5	11.5	51.4	26.5	24.9	-5.6	-1.6	-1.6	25.6	25.0	25.0	-8.7	-7.3	-7.3
900	33.1	15.2	13.4	9.9	11.6	11.6	54.7	27.1	25.3	-6.1	-1.4	-1.4	25.7	25.2	25.2	-8.8	-7.2	-7.2
1000	35.3	15.5	13.5	9.7	11.6	11.6	57.9	27.7	25.8	-6.6	-1.2	-1.2	25.8	25.3	25.3	-9.0	-7.1	-7.1
1500	46.2	16.9	13.9	8.8	11.6	11.6	73.5	30.8	27.8	-9.4	-0.8	-0.8	25.9	25.4	25.4	-10.1	-6.8	-6.8

Table S4. Fitting parameters for reverse reaction rate constants of steps 1–3 of R1 and R2[a]

	ln A	n	T_0	E
R1, Step –1	-28.628	1.590	192.730	1.339
R1, Step –2	-32.329	3.950	89.074	14.210
R1, Step –3	25.200	1.710	79.084	17.420
R2, Step –1	-30.599	3.710	277.520	1.202
R2, Step –2	-43.372	4.930	102.870	17.320
R2, Step –3	22.279	3.200	93.967	23.880

[a] The units of A for bimolecular reverse steps are cm^3 $molecule^{-1}$ s^{-1} and s^{-1} for unimolecular reverse steps; the parameters T_0 and E are in units of K and kcal/mol respectively, and n is unitless.

Table S5. Equilibrium constants (unitless) for step1–3 of R1 and R2 at various temperatures

T/K	R1–Step1	R1–Step2	R1–Step3	R2–Step1	R2–Step2	R2–Step3
298	1.05×10^{-14}	3.31×10^{15}	1.15×10^{1}	8.76×10^{-9}	7.56×10^{10}	2.19×10^{3}
300	1.30×10^{-14}	2.66×10^{15}	1.13×10^{1}	1.01×10^{-8}	6.40×10^{10}	2.06×10^{3}
400	1.99×10^{-11}	6.87×10^{11}	6.45	1.26×10^{-6}	1.22×10^{8}	2.26×10^{2}
500	1.83×10^{-9}	4.98×10^{9}	4.60	2.28×10^{-5}	3.26×10^{6}	5.79×10^{1}
600	4.01×10^{-8}	1.88×10^{8}	3.68	1.57×10^{-4}	3.16×10^{5}	2.29×10^{1}
700	3.86×10^{-7}	1.80×10^{7}	3.14	6.23×10^{-4}	6.22×10^{4}	1.17×10^{1}
800	2.19×10^{-6}	3.11×10^{6}	2.80	1.76×10^{-3}	1.89×10^{4}	7.00
900	8.66×10^{-6}	7.86×10^{5}	2.56	3.94×10^{-3}	7.60×10^{3}	4.68
1000	2.67×10^{-5}	2.60×10^{5}	2.38	7.52×10^{-3}	3.71×10^{3}	3.37
1500	9.03×10^{-4}	8.87×10^{3}	1.92	5.25×10^{-2}	4.51×10^{2}	1.24

Table S6. Classical barrier heights and reaction energies (kcal/mol) computed by G4 and M08–HX/MG3S methods for all the steps in reaction R1. Mean unsigned deviations (MUDs, in kcal/mol) are computed of each method with respect to the other. MUD1 is for all energies; MUD2 is for all ΔE values; MUD3 is for all forward barriers V_f.

	G4	M08-HX/MG3S
Step1 V_f	19.59	21.08
V_r	1.06	1.43
ΔE	18.53	19.65
Step2 V_f	0.54	1.06
V_r	22.7	22.28
ΔE	-22.16	-21.22
Step3 V_f	22.28	23.04
V_r	23.44	24.59
ΔE	-1.16	-1.55
Overall ΔE	-4.8	-3.11
MUD1	0.89	
MUD2	1.04	
MUD3	0.93	

Table S6 shows a comparison to the G4 method,[1] which was requested by a reviewer. The G4 method is a wave function method with six empirical parameters; it uses geometries optimized by B3LYP, which has been found[2,3] to be unreliable for transition state geometries. Furthermore the optimization is accomplished with small basis set (6-31G(2df,p)). Nevertheless, the table shows that the G4 results agree with M08-HX/MG3S ones within about 1 kcal/mol.

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