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Supporting Information

An unprecedented condensation reaction of gas-phase silyl cations mediated by a bissilylated chloronium ion intermediate

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Calculated Cartesian coordinates for optimized geometries and energetics for reactants, intermediates, transition states and products of the reaction between $SiCl_2(OH)^+$ and $SiCl_4$, see Fig. 1.

Theoretical calculations were carried out with the Gaussian 03 suite of programs [1] at the MP2/6-311+G(d,p) level theory and vibrational frequencies corrected by a constant factor 0.9523 to estimate the zero points energies [2].

Table 1 – Cartesian coordinates of $SiCl_2OH^+$ (in Å).

Atomic number	X	Y	Z
14	0.003568	0.345082	0.000000
17	1.714333	-0.588103	0.000000
17	-1.673733	-0.632515	0.000000
8	-0.117758	1.915333	0.000000
1	0.565402	2.598543	0.000000

Table 2 – Calculated energetics for $SiCl_2OH^+$.

Thermodynamic quantities	(Hartree/Particle)
Zero-point correction	0.017564
Thermal correction to Energy	0.022741
Thermal correction to Enthalpy	0.023685
Thermal correction to Gibbs Free Energy	-0.012078
Sum of electronic and zero-point Energies	-1283.790719
Sum of electronic and thermal Energies	-1283.785542
Sum of electronic and thermal Enthalpies	-1283.784597
Sum of electronic and thermal Free Energies	-1283.820360

Table 3 – Cartesian coordinates of $SiCl_4$ (in Å).

Atomic number	X	Y	Z
14	0.000000	0.000000	0.000000
17	1.166365	-1.166365	1.166365
17	1.166365	1.166365	-1.166365
17	-1.166365	1.166365	1.166365
17	-1.166365	-1.166365	-1.166365

Table 4 – Calculated energetics for $SiCl_4$.

Thermodynamic quantities	(Hartree/Particle)
Zero-point correction	0.007242
Thermal correction to Energy	0.013735
Thermal correction to Enthalpy	0.014679
Thermal correction to Gibbs Free Energy	-0.022983
Sum of electronic and zero-point Energies	-2127.794407
Sum of electronic and thermal Energies	-2127.787915
Sum of electronic and thermal Enthalpies	-2127.786971
Sum of electronic and thermal Free Energies	-2127.824633

Table 5 – Cartesian coordinates of RC (in Å).

Atomic number	X	Y	Z
14	-2.046535	-0.036751	-0.381966
17	-2.494900	1.388436	0.925412
17	-1.713122	-1.823814	0.403886
8	-2.906424	-0.112318	-1.721808
1	-3.431648	0.578930	-2.136198
14	1.673665	0.072748	0.076893
17	1.042250	0.418431	1.931033
17	3.047111	1.335947	-0.584757
17	2.039221	-1.836857	-0.313075
17	-0.057524	0.581521	-1.210101

Table 6 – Calculated energetics for RC.

Thermodynamic quantities	(Hartree/Particle)
Zero-point correction	0.025978
Thermal correction to Energy	0.039341
Thermal correction to Enthalpy	0.040285
Thermal correction to Gibbs Free Energy	-0.017304
Sum of electronic and zero-point Energies	-3411.625943
Sum of electronic and thermal Energies	-3411.612580
Sum of electronic and thermal Enthalpies	-3411.611636
Sum of electronic and thermal Free Energies	-3411.669225

Table 7 – Cartesian coordinates of TS1 (in Å).

Atomic number	X	Y	Z
14	1.761732	-0.048639	-0.027673
17	2.718781	1.677179	-0.213595
17	0.420899	-0.016337	1.561525
17	2.939711	-1.642058	0.001026
8	0.480198	-0.205106	-1.086747
1	0.576690	-0.399061	-2.029498
14	-1.602692	0.025651	-0.118936
17	-1.571027	1.903372	-0.758174
17	-2.067329	-1.442772	-1.383113
17	-2.741466	-0.187281	1.506628

Table 8 – Calculated energetics for TS1.

Thermodynamic quantities	(Hartree/Particle)
Zero-point correction	0.026320
Thermal correction to Energy	0.038760
Thermal correction to Enthalpy	0.039705
Thermal correction to Gibbs Free Energy	-0.015941
Sum of electronic and zero-point Energies	-3411.608373
Sum of electronic and thermal Energies	-3411.595933
Sum of electronic and thermal Enthalpies	-3411.594988
Sum of electronic and thermal Free Energies	-3411.650634

Table 9 – Cartesian coordinates of Int (in Å).

Atomic number	X	Y	Z
14	1.659709	0.023572	-0.053568
17	2.096488	1.896909	-0.536179
17	1.457909	-0.294639	1.895449
17	2.716211	-1.344454	-1.038706
8	0.005280	-0.263601	-0.706528
1	0.012570	-0.692519	-1.582136
14	-1.659705	0.065195	-0.101711
17	-2.693692	0.118770	-1.800594
17	-2.102294	-1.467551	1.076370
17	-1.482151	1.801263	0.844409

Table 10 – Calculated energetics for Int.

Thermodynamic quantities	(Hartree/Particle)
Zero-point correction	0.027337
Thermal correction to Energy	0.040176
Thermal correction to Enthalpy	0.041120
Thermal correction to Gibbs Free Energy	-0.015535
Sum of electronic and zero-point Energies	-3411.661359
Sum of electronic and thermal Energies	-3411.648520
Sum of electronic and thermal Enthalpies	-3411.647576
Sum of electronic and thermal Free Energies	-3411.704231

Table 11 – Cartesian coordinates of TS2 (in Å).

Atomic number	X	Y	Z
14	1.590306	-0.027102	0.025841
17	2.083868	-0.789747	1.773280
17	2.246677	-0.965309	-1.575096
17	2.024527	2.098225	-0.066509
8	0.004370	0.496643	-0.076088
1	0.605613	1.741825	-0.108180
14	-1.632717	-0.035575	-0.009344
17	-2.332610	0.588040	1.750645
17	-2.529200	0.830971	-1.562756
17	-1.511604	-2.030404	-0.151487

Table 12 – Calculated energetics for TS2.

Thermodynamic quantities	(Hartree/Particle)
Zero-point correction	0.021958
Thermal correction to Energy	0.034374
Thermal correction to Enthalpy	0.035318
Thermal correction to Gibbs Free Energy	-0.021926
Sum of electronic and zero-point Energies	-3411.622611
Sum of electronic and thermal Energies	-3411.610196
Sum of electronic and thermal Enthalpies	-3411.609252
Sum of electronic and thermal Free Energies	-3411.666496

Table 13 – Cartesian coordinates of PC (in Å).

Atomic number	X	Y	Z
14	1.622919	-0.117932	0.174113
17	2.368033	0.299016	1.954797
17	2.734147	-1.268186	-0.978355
17	1.597704	1.873115	-0.912123
8	0.059965	-0.422760	0.147385
1	0.278433	2.035824	-0.791072
14	-1.574490	-0.173678	0.130107
17	-2.313131	-0.404864	1.960699
17	-1.695444	1.808382	-0.445967
17	-2.406184	-1.348629	-1.239167

Table 14 – Calculated energetics for PC.

Thermodynamic quantities	(Hartree/Particle)
Zero-point correction	0.024147
Thermal correction to Energy	0.037013
Thermal correction to Enthalpy	0.037957
Thermal correction to Gibbs Free Energy	-0.020172
Sum of electronic and zero-point Energies	-3411.641588
Sum of electronic and thermal Energies	-3411.628722
Sum of electronic and thermal Enthalpies	-3411.627778
Sum of electronic and thermal Free Energies	-3411.685907

Table 15 – Cartesian coordinates of $Cl_3SiOSiCl_2^+$ (in Å).

Atomic number	X	Y	Z
14	1.792950	-0.017976	0.068025
17	2.736002	1.665443	-0.210269
17	2.813695	-1.669703	0.234757
8	0.241353	-0.047157	0.159700
14	-1.459138	-0.001500	0.000239
17	-2.162846	-0.111729	1.861251
17	-1.862416	1.735534	-0.899061
17	-1.919888	-1.587144	-1.121469

Table 16 – Calculated energetics for $Cl_3SiOSiCl_2^+$.

Thermodynamic quantities	(Hartree/Particle)
Zero-point correction	0.014778
Thermal correction to Energy	0.025806
Thermal correction to Enthalpy	0.026750
Thermal correction to Gibbs Free Energy	-0.030774
Sum of electronic and zero-point Energies	-2951.368771
Sum of electronic and thermal Energies	-2951.357744
Sum of electronic and thermal Enthalpies	-2951.356800
Sum of electronic and thermal Free Energies	-2951.414323

Table 17 – Cartesian coordinates of HCl (in Å).

Atomic number	X	Y	Z
17	0.000000	0.000000	0.008471
1	0.000000	0.000000	1.281529

Table 18 – Calculated energetics for HCl.

Thermodynamic quantities	(Hartree/Particle)
Zero-point correction	0.006697
Thermal correction to Energy	0.009057
Thermal correction to Enthalpy	0.010001
Thermal correction to Gibbs Free Energy	-0.011193
Sum of electronic and zero-point Energies	-460.238006
Sum of electronic and thermal Energies	-460.235646
Sum of electronic and thermal Enthalpies	-460.234702
Sum of electronic and thermal Free Energies	-460.255896

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