JO0343681

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TITLE: Methyl and Silyl Mesolytic Dissociations in the Radical Cations and Radical Anions of But-1-ene, Allylsilane, Hexa-1,3-diene, and Penta-2,4-dienylsilane. CAS-MCSCF and Coupled Cluster Theoretical Study

SUPPLEMENTARY INFORMATION

CONTENT:

GEOMETRIES (cartesian coordinates of the critical points) AND ENERGIES

#n CASSCF(3,4)/6-31g*

but-1-ene radical cation: Reactant -

1,2

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.468400
C	1.156756	0.000000	2.272184
H	0.974184	-0.237837	-0.403950
H	-0.730146	-0.722852	-0.349950
H	-0.951867	0.037487	1.973221
H	1.082403	0.016519	3.343580
H	2.134321	-0.021004	1.825954
C	-0.462979	1.431268	-0.503143
H	-1.454185	1.671621	-0.141644
H	0.233091	2.199771	-0.194280
H	-0.485049	1.395226	-1.583317

CASSCF= -155.8290662936
CCSD(T)/6-311G* = -156.40570625

#n CASSCF(3,4)/6-31g*

but-1-ene radical cation: Separated fragments

1,2

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.378498
C	1.207086	0.000000	2.042896
H	0.918049	-0.003837	-0.560132
H	-0.917145	0.007962	-0.560995
H	-0.924899	0.008202	1.924984
H	1.256151	0.007407	3.116913
H	2.140178	-0.007260	1.508186
C	-0.038593	4.592804	-2.184971
H	-0.926845	4.965670	-1.710987
H	0.909910	4.976439	-1.859484
H	-0.117319	4.217645	-3.187810

CASSCF = -155.7792613904
CCSD(T)/6-311G* = -156.33837856

#n CASSCF(3,4)/6-31g*

allylsilane radical cation: Reactant -

1,2

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.398817
C	1.164072	0.000000	2.195435
H	0.913284	-0.281389	-0.505613
H	-0.909172	-0.323782	-0.487018
H	-0.949195	0.038988	1.907147
H	1.092133	0.005909	3.265258
H	2.140267	-0.027453	1.749077
Si	-0.106654	2.073619	-0.408285
H	-1.308501	2.550471	0.269456
H	1.140772	2.632096	0.104768
H	-0.202164	1.999836	-1.862447

CASSCF= -406.8847379882
CCSD(T)/6-311G* = -407.42812279

#n CASSCF(3,4)/6-31g*

allylsilane radical cation: Separated fragments

1,2

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.378653
C	1.206806	0.000000	2.043618
H	0.918270	0.000394	-0.559773
H	-0.917127	-0.000383	-0.561026
H	-0.925144	-0.000276	1.924809
H	1.255250	-0.001420	3.117684
H	2.140261	0.001174	1.509474
Si	-0.280738	4.692050	-1.704656
H	-0.923659	5.462343	-0.626536
H	1.108943	5.120863	-1.936262
H	-1.078649	4.687007	-2.940911

CASSCF= -406.8281284655
CCSD(T)/6-311G* = -407.35064033

#n CASSCF(5,6)/6-31g*

- esa-1,3-dienyl radical cation: Reactant -

1,2

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.483819
C	1.137729	0.000000	2.285911
H	1.009062	-0.049279	-0.388735
H	-0.535031	-0.888005	-0.328714
H	-0.959084	0.009971	1.975827
H	2.106637	-0.004746	1.817508
C	1.052482	0.001085	3.680030
C	-0.744899	1.263712	-0.565015
H	-1.770031	1.299168	-0.216242
H	-0.240016	2.176331	-0.273144
H	-0.752241	1.205215	-1.645089
H	0.081664	0.005461	4.143609
C	2.180765	-0.005173	4.484019
H	3.167316	-0.010350	4.059452
H	2.097768	-0.004857	5.553589

CASSCF= -232.7793056064
CCSD(T)/6-311G*= -233.63917214

#n CASSCF(5,6)/6-31g*

- esa-1,3-dienyl radical cation: Separated fragments

1,2

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.361231
C	1.229411	0.000000	2.052787
H	0.916117	-0.001258	-0.562469
H	-0.916979	0.001071	-0.558523
H	-0.920326	0.001275	1.915955
H	2.133474	-0.001169	1.465832
C	1.355898	0.001549	3.457732
C	4.863803	0.014453	-1.158969
H	5.531657	0.567538	-0.525807
H	4.981297	-1.051318	-1.214530
H	4.427874	0.521940	-1.998771
H	0.469340	0.003368	4.065235
C	2.591693	0.000463	4.028521
H	3.487457	-0.001678	3.434446
H	2.713130	0.001511	5.095243

CASSCF = -232.7273285678
CCSD(T)/6-311G*= -233.56673336

#n CASSCF(5,6)/6-31g*

radical cation of penta-2,4-dienylsilane: Reactant -

1,2

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.438742
C	1.146509	0.000000	2.242051
H	0.909965	-0.390860	-0.439786
H	-0.876886	-0.483831	-0.414952
H	-0.952900	0.048360	1.940223
H	2.111795	-0.046119	1.768414
C	1.069154	0.040228	3.638068
Si	-0.147156	1.894061	-0.656219
H	-1.366914	2.463304	-0.074247
H	1.054154	2.598412	-0.193951
H	-0.210772	1.764744	-2.112330
H	0.099434	0.084497	4.102287
C	2.194838	0.018579	4.439388
H	3.180835	-0.027801	4.016199
H	2.113306	0.047112	5.508381

CASSCF= -483.8253584816
CCSD(T)/6-311G* = -484.64820272

#n CASSCF(5,6)/6-31g*

radical cation of penta-2,4-dienylsilane: Separated fragments

1,2

C	0.100889	1.635506	0.389166
C	1.160624	1.166878	-0.326232
C	2.000425	0.177857	0.224701
C	3.120396	-0.372898	-0.432502
C	3.872538	-1.324853	0.185161
Si	-4.382388	-0.528837	-0.075419
H	-0.119387	1.271640	1.376237
H	-0.552861	2.387361	-0.010719
H	1.366877	1.541844	-1.312058
H	1.771843	-0.181262	1.214299
H	-4.801286	-1.668322	-0.907870
H	-4.412176	-0.862066	1.361157
H	-5.165027	0.685759	-0.363018
H	3.369276	-0.031639	-1.420740
H	3.637454	-1.677598	1.172897
H	4.729481	-1.756935	-0.296078

CASSCF = 483.7745214256
CCSD(T)/6-311g* = -484.57651019

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#n CASSCF(5,4)/6-31g*

- but-1-ene radical anion: Reactant -

-1,2

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.511813
C	1.272390	0.000000	2.188173
H	0.632555	-0.813488	-0.369331
H	-1.002370	-0.199179	-0.396058
H	-0.748937	0.683830	1.923022
H	1.232723	0.015463	3.279714
H	1.995585	-0.745877	1.840195
C	0.517480	1.321234	-0.681461
H	-0.132539	2.155752	-0.422510
H	1.509878	1.546568	-0.307290
H	0.554129	1.249593	-1.773577

CASSCF = -155.992897222
CCSD(T)/6-311+G* = -156.67282651

#n CASSCF(5,4)/6-31g*

- but-1-ene radical anion: TS -

-1,2

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.406962
C	1.073254	0.000000	2.293916
H	0.905432	-0.311273	-0.502341
H	-0.896747	-0.338190	-0.497784
H	-0.981519	0.083059	1.867646
H	0.930223	0.222370	3.341331
H	2.094545	0.019208	1.939929
C	0.000210	2.040681	-1.085213
H	-0.923195	2.526938	-0.789032
H	0.868469	2.533800	-0.665185
H	0.072863	1.933638	-2.166889

CASSCF = -155.9584729903
CCSD(T)/6-311+G* = -156.63226902

#n CASSCF(5,4)/6-31g*

- but-1-ene radical anion: Separated fragments

-1,2

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.389587
C	1.022208	0.000000	2.336349
H	0.925927	0.107447	-0.553662
H	-0.897650	0.276176	-0.538899
H	-0.999808	0.022537	1.826393
H	0.800563	-0.286262	3.357588
H	2.051015	-0.156193	2.029337
C	2.264055	5.140094	1.103995
H	1.412581	5.755500	0.879619
H	2.113830	4.262614	1.703299
H	3.083139	5.164533	0.409780

CASSCF = -155.9700727108
CCSD(T)/6-311+G* = -156.62573946

#n CASSCF(7,6)/6-31g*

allylsilane radical anion: Reactant -

-1,2

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.485000
C	1.068575	0.000000	2.305260
H	0.977712	-0.280746	-0.389662
H	-0.727159	-0.715619	-0.383136
H	-0.974030	0.089497	1.948047
H	0.966046	0.102004	3.374019
H	2.075304	-0.062429	1.923756
Si	-0.524119	1.850103	-0.806264
H	-0.883264	3.080408	-1.750124
H	-1.858326	1.921335	-0.030080
H	0.505992	2.616982	-0.005926

CASSCF = -407.0935523545
CCSD(T)/6-311+G* = -407.69253786

#n CASSCF(7,6)/6-31g*

allylsilane radical anion: TS -

-1,2

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.428284
C	1.094051	0.000000	2.245160
H	0.923315	-0.205356	-0.513376
H	-0.884587	-0.332747	-0.510118
H	-0.968247	0.050443	1.905085
H	0.998188	0.071141	3.315012
H	2.094420	-0.007740	1.846221
Si	-0.307135	2.649338	-0.673020
H	-0.489641	4.053618	-1.323774
H	-1.495396	2.761510	0.275560
H	0.805695	3.052874	0.281799

CASSCF = -407.0854225794
CCSD(T)/ 6-311+G* = -407.67826935

#n CASSCF(7,6)/6-31g*

allylsilane radical anion: Separated fragments -

-1,2

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.390095
C	1.142375	0.000000	2.181526
H	0.919066	-0.008508	-0.557207
H	-0.915386	0.016526	-0.559777
H	-0.954971	-0.001900	1.890146
H	1.080324	0.003823	3.253266
H	2.123706	0.024847	1.743460
Si	-0.964160	8.865702	-4.524347
H	-1.114486	10.236525	-5.209735
H	-2.192769	9.028250	-3.610378
H	0.069233	9.361161	-3.453643

CASSCF = -407.1035842271
CCSD(T)/6-311+G* = -407.66930794

#n CASSCF(7,6)/6-31g*

- esa-1,3-dienyl radical anion: Reactant -

-1,2

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.503533
C	1.190911	0.000000	2.249043
H	0.838445	-0.592396	-0.369509
H	-0.901724	-0.478297	-0.394193
H	-0.901821	0.381083	1.971657
H	2.087135	-0.299785	1.709983
C	1.365679	0.274473	3.612661
C	0.098318	1.418846	-0.667277
H	-0.739544	2.039853	-0.357919
H	1.011077	1.913084	-0.349479
H	0.093115	1.362852	-1.758440
H	0.474593	0.604361	4.140396

C	2.516071	0.133414	4.394221
H	3.472377	-0.088487	3.939683
H	2.556648	0.555866	5.387697

CASSCF = -232.9437869797
CCSD(T)/6-311+G* = -233.87802572

#n CASSCF(7,6)/6-31g*

- esa-1,3-dienyl radical anion: TS -

-1,2

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.391900
C	1.095179	0.000000	2.272975
H	0.898475	-0.287158	-0.525184
H	-0.913743	-0.242145	-0.518817
H	-0.974802	0.093715	1.861571
H	2.089720	-0.088909	1.853088
C	0.981731	0.096336	3.682640
C	0.081143	2.189191	-1.030582
H	-0.861978	2.627729	-0.745706
H	0.937193	2.580850	-0.508234
H	0.214444	2.051921	-2.095021
H	-0.035164	0.189822	4.051619
C	1.959298	0.084871	4.641825
H	3.005408	-0.002415	4.390980
H	1.719303	0.167468	5.689314

CASSCF = -232.8965216793
CCSD(T)/6-311+G* = 233.87802572

#n CASSCF(7,6)/6-31g*

- esa-1,3-dienyl radical anion: separated fragments -

-1,2

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.369655
C	1.070633	0.000000	2.294629
H	0.912176	-0.095911	-0.570817
H	-0.922032	-0.048611	-0.558002
H	-0.985574	0.040720	1.827258
H	2.082222	-0.066127	1.913416
C	0.881192	0.060062	3.696088
C	3.268669	8.746502	-3.579736
H	2.291497	9.097803	-3.309093
H	3.927316	8.477007	-2.776683
H	3.432625	8.339828	-4.558061
H	-0.159419	0.126558	4.004161
C	1.786940	0.046057	4.722272
H	2.850258	-0.028419	4.548506
H	1.468664	0.088804	5.751862

CASSCF = -232.9096808691
CCSD(T)/6-311+G* = -233.84124113

#n CASSCF(7,6)/6-31g*

radical anion of penta-2,4-dienylsilane: Reactant -

-1,2

6	1.227930	1.059395	-0.200853
14	2.626876	-0.518971	-0.055951
6	-0.069850	0.681539	0.383131
6	-1.195465	0.311542	-0.277925
6	-2.400387	-0.170428	0.384080
6	-3.557067	-0.509080	-0.220878
1	1.134508	1.340188	-1.247784
1	1.678156	1.890142	0.338063
1	-0.086378	0.591372	1.461838
1	-1.221538	0.370727	-1.355877
1	2.492686	-0.610087	1.450925
1	1.700926	-1.551817	-0.650651
1	3.919452	-1.430570	-0.126518
1	-2.344292	-0.260937	1.458970
1	-3.674764	-0.449540	-1.290170
1	-4.405986	-0.861683	0.339192

CASSCF = -483.9994399984
CCSD(T)/6-311+G* = -484.89375938

#n CASSCF(7,6)/6-31g*

radical anion of penta-2,4-dienylsilane: TS -

-1,2

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.410391
C	1.102873	0.000000	2.246501
H	0.908306	-0.254284	-0.518378
H	-0.899910	-0.289694	-0.509452
H	-0.965797	0.080643	1.890468
H	2.088692	-0.056945	1.810604
C	1.011987	0.071613	3.679997

Si	-0.146260	2.530994	-0.614151
H	-1.330342	2.718955	0.310813
H	1.005330	2.895566	0.291537
H	-0.268991	3.857277	-1.388240
H	0.014563	0.168263	4.084844
C	2.041401	0.032370	4.562838
H	3.064366	-0.052447	4.236020
H	1.876115	0.100213	5.624018

CASSCF = -483.99208061
CCSD(T)/6-311+G* -484.88694404

#n CASSCF(7,6)/6-31g*

radical anion of penta-2,4-dienylsilane:
Separated fragments

-1,2

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.367111
C	1.170568	0.000000	2.173420
H	0.912069	0.005229	-0.568772
H	-0.908986	0.002767	-0.570133
H	-0.948807	0.000262	1.881862
H	2.127281	-0.001216	1.677827
C	1.152213	0.004166	3.594715
Si	-0.042087	0.101948	-4.998783
H	-1.028464	-0.316718	-3.889592
H	1.129054	0.391614	-4.039302
H	-0.526931	1.559997	-5.077565
H	0.184245	0.007807	4.071562
C	2.262906	0.005016	4.391767
H	3.254080	0.001058	3.973730
H	2.184708	0.009616	5.463372

CASSCF = -484.0150220955
CCSD(T)/6-311+G* -484.87570919

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#n CASSCF(4,4)/6-31g*

- but-1-ene -

0,1

C	-0.576469	0.441799	0.365787
C	0.726292	0.262066	-0.367065
C	1.871816	-0.151806	0.189354
H	-0.439460	0.224958	1.420998
H	-0.893540	1.480023	0.294693
H	0.709306	0.481021	-1.424061
H	2.771433	-0.264925	-0.388950
H	1.940541	-0.384773	1.238361
C	-1.709076	-0.464469	-0.204990
H	-1.879861	-0.252631	-1.256267
H	-1.444248	-1.512495	-0.111063
H	-2.639548	-0.296717	0.327772

CCSD(T)/6-311g* = -156.74914607
CCSD(T)/6-311+g* = -156.75237945

#n CASSCF(4,4)/6-31g*

- allylsilane -

0,1

C	-0.115884	-0.677000	-0.465502
C	-0.108559	-0.824495	1.033992
C	0.972291	-1.094733	1.778164
H	0.813606	-1.049469	-0.889101
H	-0.918578	-1.271943	-0.897056
H	-1.054183	-0.670887	1.529888
H	0.911712	-1.168227	2.849059
H	1.940907	-1.255493	1.336384
Si	-0.352844	1.148446	-1.032837
H	-1.577555	1.715329	-0.428207
H	0.821428	1.986959	-0.616329
H	-0.484608	1.212859	-2.504833

CCSD(T)/6-311g* = -407.74855952
CCSD(T)/6-311+g* = -407.75251665

#n CASSCF(6,6)/6-31g*

- esa-1,3-diene -

0,1

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.504657
C	1.100899	0.000000	2.277031
H	1.019867	-0.042308	-0.371163
H	-0.504462	-0.892851	-0.363365
H	-0.969898	0.008074	1.980293
H	2.074326	-0.004908	1.811299
C	1.075872	0.003170	3.742075
C	-0.713642	1.251174	-0.594852
H	-1.743984	1.305662	-0.255793
H	-0.209705	2.161905	-0.287955
H	-0.718346	1.210833	-1.679495

H 0.103494 0.007054 4.207854
C 2.174398 0.001675 4.516493
H 3.164646 -0.002315 4.094429
H 2.107214 0.004182 5.588999

CCSD(T)/6-311g* = -233.94064536
CCSD(T)/6-311+g* = -233.94593943

#n CASSCF(6,6)/6-31g*

- penta-2,4-dienylsilane -

0,1
C 0.000000 0.000000 0.000000
C 0.000000 0.000000 1.505492
C 1.100699 0.000000 2.280054
H 0.990124 -0.236729 -0.381741
H -0.672429 -0.769008 -0.375755
H -0.968200 0.027697 1.981741
H 2.074724 -0.025307 1.816564
C 1.071046 0.025106 3.744073
Si -0.547155 1.689300 -0.745291
H -1.866319 2.082224 -0.205682
H 0.432931 2.741971 -0.409885
H -0.652119 1.590830 -2.217283
H 0.097455 0.046260 4.206624
C 2.166619 0.022593 4.523046
H 3.158135 0.003757 4.104666
H 2.094484 0.040595 5.595014

CCSD(T)/6-311g* = -484.94021637
CCSD(T)/6-311+g* = -484.94626731

Selected geometrical parameters for the a–$XH_3^{\bullet+}$ and a–$XH_3^{\bullet-}$ reactants

q:	C-X / Å	%Δq	<CCX / °	%Δq	C=C/ Å	%Δq
X=C (1)						
CH_3 cation	1.586	+2	108.5	-3	1.409	+5
CH_3 anion	1.574	+1	115.6	+3	1.441	+8
CH_3 neutral	1.559	0	112.4	0	1.339	0
X=Si (2)						
SiH_3 cation	2.116	+10	101.1	-10	1.410	+5
SiH_3 anion	2.085	+8	112.7	0	1.347	+1
SiH_3 neutral	1.926	0	112.7	0	1.340	0

(1) these %Δq reflect the depopulation of a mainly π HOMO, or the population of a mainly π LUMO

(2) here the Si- centered group prevails to some extent in both HOMO and LUMO

Selected geometrical parameters for p–$XH_3^{\bullet+}$ and p–$XH_3^{\bullet-}$ reactants

X-CH_2-C^2H=C^3H-C^4H=C^5H_2

q:	C-X / Å	%Δq	<CCX / °	%Δq	C^2=C^3/ Å	%Δq	C^3-C^4/ Å	%Δq	C^4=C^5/ Å	%Δq
X=C (3)										
CH_3 cation	1.572	+1	111.1	-1	1.392	+3	1.397	-5	1.385	+3
CH_3 anion	1.571	+1	115.1	+2	1.405	+4	1.402	-4	1.398	+4
CH_3 neutral	1.558	0	112.4	0	1.345	0	1.465	0	1.344	0
X=Si										
SiH_3 cation	2.010	+4	109.1	-3	1.400	+4	1.399	-4	1.382	+3
SiH_3 anion (4)	2.114	+10	111.4	-1	1.357	+1	1.457	0	1.348	0
SiH_3 neutral	1.926	0	112.8	0	1.346	0	1.464	0	1.344	0

(3) these %Δq reflect the depopulation of a HOMO, or the population of a LUMO, in which the π component prevails to a degree.

(4) here the Si- centered group prevails to some extent in the LUMO

CAS-PT2 data

SBS = 6-31G(d) BSd = 6-311G(2d,p) +BSd = 6-311+G(2d,p)

1-Butene Radical Cation CAS(3,4)

	CAS/SBS	CAS/BSd//SBS	PT2(FC)/BSd //CAS/SBS	CCSD(T)/BSd //CAS/SBS
Minimum	-155.829073	-155.873212	-156.420895	
Rcc = 10.	-155.777832	-155.825916	-156.352721	
DeltaE(kcal mole-1)	32.15	29.68	42.78	42.5

1-Butene Radical Anion CAS(5,4)

	CAS/SBS	CAS/+BSd//SBS	PT2(FC)/+BSd //CAS/SBS	CCSD(T)/+BSd //CAS/SBS
Minimum	-155.992897	-156.065431	-156.707041	
Rcc = 10.	-155.969024	-156.046172	-156.656603	
DeltaE(kcal mole-1)	14.98	12.09	31.65	29.0

AllylSilane Radical Cation CAS(3,4)

	CAS/SBS	CAS/BSd//SBS	PT2(FC)/BSd //CAS/SBS	CCSD(T)/BSd //CAS/SBS
Minimum	-406.884742	-406.946686	-407.456879	
Rcsi = 10.	-406.827444	-406.890624	-407.371677	
DeltaE(kcal mole-1)	35.96	35.18	53.47	49.7

AllylSilane Radical Anion CAS(5,4)

	CAS/SBS	CAS/+BSd//SBS	PT2(FC)/+BSd //CAS/SBS	CCSD(T)/+BSd //CAS/SBS
Minimum	-407.079606	-407.155078	-407.726995	
Rcsi = 10.	-407.089937	-407.161794	-407.703912	
DeltaE(kcal mole-1)	-6.48	-4.21	14.48	12.9

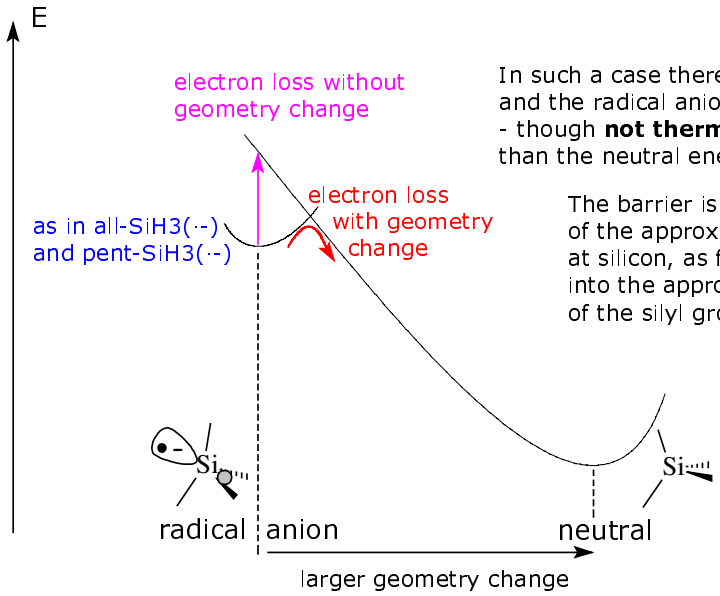
AllylSilane Radical Anion CAS(7,6)

	CAS/SBS	CAS/+BSd//SBS	PT2(FC)/+BSd //CAS/SBS	CCSD(T)/+BSd //CAS/SBS
Minimum	-407.094453	-407.169520	-407.726321	
Rcsi = 10.	-407.103863	-407.174720	-407.706999	
DeltaE(kcal mole-1)	-5.90	-3.26	12.12	12.9

Dissociation Profile - AllylSilane Radical Anion CAS(7,6)

	CAS-MCSCF/6-31G(d)		CAS-MCSCF/6-311+G(d) //6-31G(d)		PT2(FC)/ 6-311+G(d) //CAS-MCSCF/6-31G(d)	
	a.u.	Kcal	a.u.	Kcal	a.u.	Kcal
Minimum	-407.094453	0.00	-407.148533	0.00	-407.621633	0.00
Rcsi = 2.50	-407.088650	+3.64	-407.140495	+5.04	-407.614793	+4.29
Rcsi = 2.75	-407.085420	+5.67	-407.136526	+7.54	-407.609650	+7.52
Rcsi = 2.90	-407.090639	+2.39	-407.141379	+4.49	-407.603773	+11.21
Rcsi = 2.95	-407.092058	+1.50	-407.142815	+3.59	-407.603615	+11.31
Rcsi = 3.00	-407.093404	+0.66	-407.144166	+2.74	-407.603743	+11.23
Rcsi = 3.05	-407.095840	-0.87	-407.146225	+1.20	-407.604678	+10.64
Rcsi = 3.10	-407.097142	-1.69	-407.147473	+0.67	-407.605246	+10.28
Rcsi = 3.20	-407.099470	-3.15	-407.149691	-0.73	-407.606370	+9.58
Rcsi = 3.50	-407.104330	-6.20	-407.154869	-3.98	-407.608370	+8.32
Rcsi = 4.00	-407.106555	-7.59	-407.157408	-5.57	-407.608952	+8.18
Rcsi = 5.00	-407.105704	-7.06	-407.156642	-5.09	-407.606767	+9.33
Rcsi = 7.50	-407.104304	-6.18	-407.155234	-4.20	-407.603998	+11.07
Rcsi = 10.	-407.103863	-5.90	-407.154737	-3.89	-407.603394	+11.45

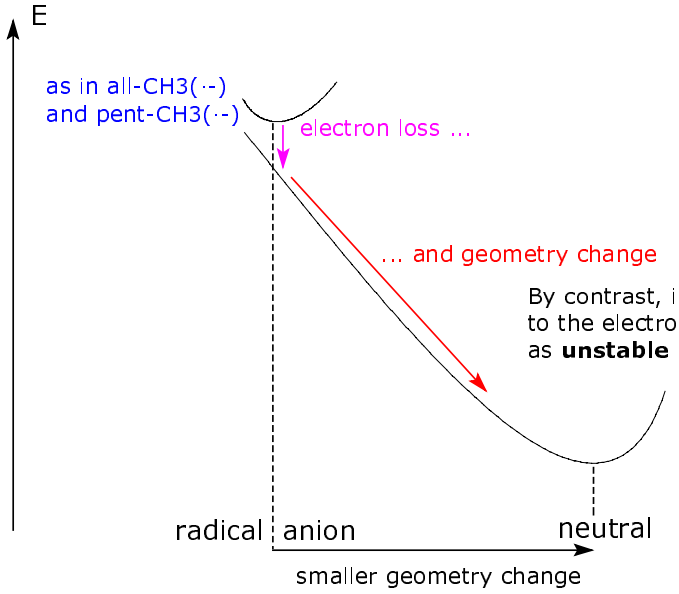
STABILITY OF THE RADICAL ANIONS



1

In such a case there should be a barrier to the electron loss and the radical anion could be defined as **kinetically stable** - though **not thermodinamically**, because its energy is higher than the neutral energy.

The barrier is related to the transformation of the approximately trigonal bipyramidal arrangement at silicon, as found for the radical anion, into the approximately locally tetrahedral geometry of the silyl group in the neutral.



2

By contrast, in such a case there should be no barrier to the electron loss, and the radical anion could be defined as **unstable both kinetically and thermodinamically**.

Methyl and Silyl Mesolytic Dissociations in the Radical Cations and Anions of But-1-ene, Allylsilane, Hexa-1,3-diene, and Penta-2,4-dienylsilane. CAS-MCSCF and Coupled Cluster Theoretical Study.

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