CHEMPHYSCHEM

Supporting Information

Synthesis of the Smallest Member of the Silylketene Family: $H_3SiC(H)=C=O$

György Tarczay,*[a, b] Marko Förstel,[a, c] Sándor Góbi,[a] Pavlo Maksyutenko,[a] and Ralf I. Kaiser*[a]

cphc_201601422_sm_miscellaneous_information.pdf

Table S1. Mass-to-charge ratios (*m*/*z*) and maximum intensities (*I*, background noise, integrated from *m*/*z*–0.5 to *m*/*z*+0.5) of TPD peaks (between 50 and 300 K and *m*/*z* < 106) observed by the PI-ReTOF-MS approach (using 9.60 eV photons) upon evaporation of irradiated silane – carbon monoxide ices.

SiH_4 - $^{12}C^{16}O$			SiH_4 - $^{12}C^{18}O$		
m*/*z	***I***	**Carrier**	***m*/*z***	***I***	**Carrier**
28	23	$^{28}Si^{+a}$	28	18	$^{28}Si^{+a}$
29	21	$^{29}Si^{+}$,[a] $^{28}SiH^{+a}$	29	21	$^{29}Si^{+a}$
30	13	$^{30}Si^{+}$,[a] $^{29}SiH^{+}$,[a] $^{28}SiH_2{}^{+a}$	30	11	$^{30}Si^{+}$,[a] $^{28}SiD^{+a}$
31	4	$^{30}SiH^{+}$,[a] $^{29}SiH_2{}^{+}$,[a] $^{28}SiH_3{}^{+a}$			
45	3	HCO^{+} (?)			
72	65	$H_3{}^{28}Si(H)CCO$	74	56	$H_3{}^{28}Si(H)CC^{18}O$
73	4	$H_3{}^{29}Si(H)CCO$	75	4	$H_3{}^{29}Si(H)CC^{18}O$
74	2	$H_3{}^{30}Si(H)CCO$	76	2	$H_3{}^{30}Si(H)CC^{18}O$
92	2	$^{28}Si_3H_8{}^{+}$	92	35	
93	11	$^{28}Si_2{}^{29}SiH_8{}^{+}$	93	3	
94	2	$^{28}Si^{29}Si_2H_8{}^{+}$, $^{28}Si_2{}^{30}SiH_8{}^{+}$	94	2	
102	13	metastable from $Si_4H_{10}{}^{+b}$			
103	2	metastable from $Si_4H_{10}{}^{+b}$			
104	6	metastable from $Si_4H_{10}{}^{+b}$	104	11	metastable from $Si_4H_{10}{}^{+b}$
105	2	metastable from $Si_4H_{10}{}^{+b}$			

SiH_4 - $^{13}C^{16}O$			SiD_4 - $^{12}C^{16}O$		
m*/*z	***I***	**Carrier**	***m*/*z***	***I***	**Carrier**
28	21	$^{28}Si^{+a}$	28	25	$^{28}Si^{+a}$
29	20	$^{29}Si^{+}$,[a] $^{28}SiH^{+a}$	30	31	$^{30}Si^{+}$,[a] $^{28}SiD^{+a}$
30	15	$^{30}Si^{+}$,[a] $^{29}SiH^{+}$,[a] $^{28}SiH_2{}^{+a}$	32	17	$^{30}SiD^{+}$,[a] $^{28}SiD_2{}^{+a}$
31	6	$^{30}SiH^{+}$,[a] $^{29}SiH_2{}^{+}$,[a] $^{28}SiH_3{}^{+a}$	34	3	$^{29}SiD_2{}^{+}$,[a] $^{28}SiD_3{}^{+a}$
59	4	?			
74	75	$H_3{}^{28}Si(H){}^{13}C{}^{13}CO$	76	65	$D_3{}^{28}Si(D)CCO$
75	5	$H_3{}^{29}Si(H){}^{13}C{}^{13}CO$	77	5	$D_3{}^{29}Si(D)CCO$
76	5	$H_3{}^{30}Si(H){}^{13}C{}^{13}CO$	78	3	$D_3{}^{30}Si(D)CCO$
92	35	$^{28}Si_3H_8{}^{+}$	100	12	$^{28}Si_3D_8{}^{+}$
93	5	$^{28}Si_2{}^{29}SiH_8{}^{+}$	101	2	$^{29}Si_3D_8{}^{+}$
94	2	$^{28}Si^{29}Si_2H_8{}^{+}$, $^{28}Si_2{}^{30}SiH_8{}^{+}$			
104	13	metastable from $Si_4H_{10}{}^{+b}$			
105	5	metastable from $Si_4H_{10}{}^{+b}$			

[a] From multiphoton fragmentation of $Si(H/D)_4{}^{+}$ ions or $(Si(H/D)_4)_n{}^{+}$ clusters.
[b] Mass unresolved peaks due to $Si(H/D)_4$ loss in the refrectron region.

Table S2. Cartesian geometries (in Angstrom) of the singlet SiC_2OH_4 isomers (see Fig. 3) and the transition structure (and MSX, see Fig. 5) as obtained at the B3LYP/cc-pVTZ level of theory.

Isomer 1			
C	0.000000	0.058126	0.000000
Si	0.120335	-1.755364	0.000000
H	1.547201	-2.158324	0.000000
H	-0.538649	-2.317390	1.204447
H	-0.538649	-2.317390	-1.204447
C	-0.080592	1.263099	0.000000
O	-0.085172	2.566776	0.000000
H	-0.989666	2.906640	0.000000
Isomer 2			
C	0.000000	0.657423	0.000000
C	-0.077021	1.973934	0.000000
H	-1.034491	2.479343	0.000000
H	0.823368	2.568925	0.000000
O	-1.027589	-0.313487	0.000000
Si	0.507635	-1.055922	0.000000
H	0.893537	-1.772800	1.229905
H	0.893537	-1.772800	-1.229905
Isomer 3			
C	-0.245603	-0.008883	-0.120248
Si	1.491528	-0.050327	0.084170
H	2.191670	1.188447	-0.316060
H	2.060917	-1.306786	-0.443909
O	-1.301214	0.823944	0.008329
C	-1.551308	-0.619847	0.019426
H	-1.875202	-1.006058	0.977981
H	-2.067602	-0.990191	-0.858093
Isomer 4			
C	0.351461	-0.843283	0.000000
C	1.306700	-1.937959	0.000000
H	2.318550	-1.512104	0.000000
H	1.243191	-2.566690	0.894891
H	1.243191	-2.566690	-0.894891
O	-1.561078	1.394231	0.000000
H	-2.265275	0.740185	0.000000
Si	0.000000	0.817064	0.000000
Isomer 5			
C	1.280190	1.833824	0.000000
H	1.701477	2.823254	0.000000
C	0.082871	-1.113251	0.000000
H	0.645696	-1.414257	0.888055
H	0.645696	-1.414257	-0.888055
O	-1.245752	-1.620418	0.000000
H	-1.205214	-2.581767	0.000000
Si	0.000000	0.801924	0.000000

Isomer 6

C	1.233047	0.332697	0.000000
O	2.315394	-0.083936	0.000000
C	0.000000	0.767154	0.000000
H	-0.140187	1.840617	0.000000
Si	-1.447530	-0.400646	0.000000
H	-2.292698	-0.184812	1.200884
H	-2.292698	-0.184812	-1.200884
H	-0.930435	-1.789577	0.000000

Isomer 7

C	-0.013895	1.190344	0.029271
H	-0.048778	1.768227	-0.893526
H	-0.201283	1.805649	0.906214
Si	1.142085	-0.330535	0.002861
H	1.822031	-0.731936	1.253413
H	1.962889	-0.523017	-1.212364
C	-0.743009	-0.126590	-0.046181
O	-1.872829	-0.509244	0.000959

Isomer 8

C	0.014460	-1.237638	0.000000
H	-0.064663	-1.861008	0.892790
H	-0.064663	-1.861008	-0.892790
C	1.196576	-0.264711	0.000000
O	-1.126504	-0.290911	0.000000
H	-0.368408	2.368942	0.000000
H	2.243548	-0.499876	0.000000
Si	0.000000	0.942452	0.000000

Isomer 9

H	-1.804817	-2.888201	0.000000
H	-0.441842	1.528767	1.206383
H	-0.441842	1.528767	-1.206383
O	1.637782	0.541949	0.000000
H	2.208193	1.313040	0.000000
C	-0.777232	-0.866830	0.000000
C	-1.326426	-1.939237	0.000000
Si	0.000000	0.787031	0.000000

Isomer 10

Si	-1.385227	-0.278678	0.000000
H	-2.499479	0.686953	0.000000
H	-1.388141	-1.121853	1.215076
H	-1.388141	-1.121853	-1.215076
O	0.000000	0.695676	0.000000
H	3.342926	-0.512131	0.000000
C	1.212160	0.232962	0.000000
C	2.342176	-0.165467	0.000000

Isomer 11

C	-0.938308	0.088239	-0.003583
C	1.913125	0.657852	0.001299
H	2.869503	0.197290	-0.241156
H	1.702409	1.436764	-0.727310
H	1.992990	1.106455	0.990801
O	-2.202323	0.312371	-0.106648
H	-2.627962	0.417989	0.762703
Si	0.559482	-0.723858	0.005846

Isomer 12

Si	0.000000	0.938499	0.000000
H	-0.145901	1.780300	1.209870
H	-0.145901	1.780300	-1.209870
O	-1.095741	-0.400348	0.000000
C	1.153184	-0.501122	0.000000
C	0.022472	-1.225799	0.000000
H	2.172111	-0.841903	0.000000
H	-0.168318	-2.293369	0.000000

Isomer 13

C	0.557222	-1.061174	-0.071883
H	0.921401	-1.765372	0.671461
H	0.739018	-1.433112	-1.076739
Si	-1.122160	-0.046809	0.144063
C	0.299007	1.081046	-0.102450
O	1.287041	0.208357	0.077156
H	-2.001494	-0.052074	-1.069277
H	0.617612	2.119792	-0.113576

Isomer 14

C	0.532954	-0.749817	-0.362738
C	0.532968	0.749695	-0.362953
H	1.039769	-1.387529	-1.069710
H	1.039744	1.387198	-1.070145
O	1.321610	0.000094	0.588576
Si	-1.093585	0.000017	0.089079
H	-2.154098	-0.000153	-0.944550
H	-1.583627	0.000232	1.482831

Transition structure (and MSX) in Figure 5

Si	1.55694	1.32867	0.00000
H	2.47116	0.15629	0.00000
H	1.76237	2.14816	1.22237
H	1.76237	2.14816	-1.22237
H	0.00000	0.80238	0.00000
C	-1.37006	0.21579	0.00000
C	-1.32067	-1.12769	0.00000
O	-1.45609	-2.29811	0.00000

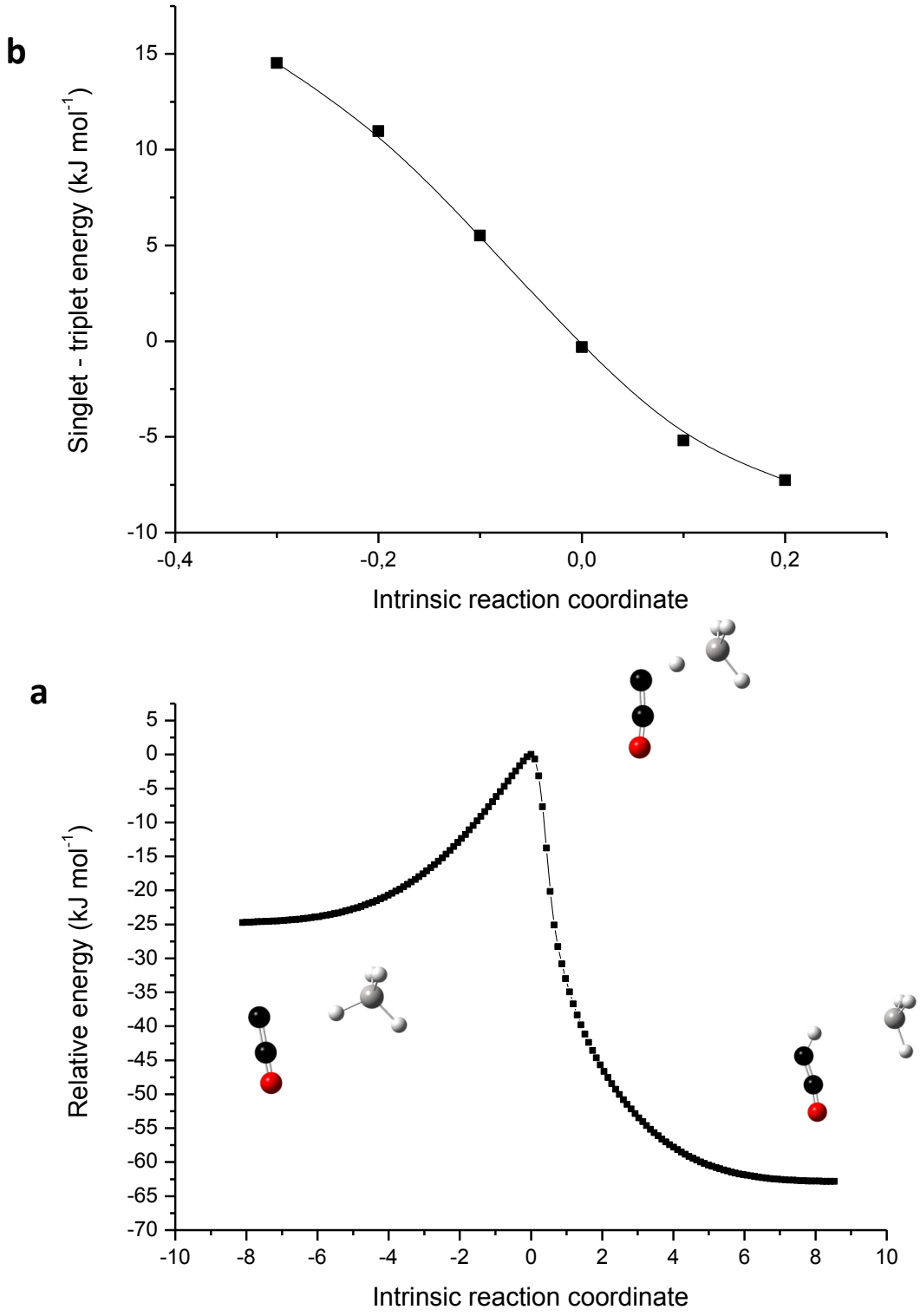

Figure S1. (a) IRC path of the $C_2O + SiH_4 \rightarrow HCCO + SiH_3$ reaction on the triplet potential energy surface as obtained at the B3LYP/cc-pVTZ level of theory. (b) Energy difference of the lowest energy singlet and triplet surfaces in the vicinity of the transition structure, along the (B3LYP/cc-pVTZ) IRC path as obtained at the fc CCSD(T)/cc-pVTZ + harmonic B3LYP/cc-pVTZ ZPVE level of theory.