Supplementary Information

The gas-phase reaction between silylene and 2-butyne: kinetics, isotope studies, pressure dependence studies and quantum chemical calculations.

Rosa Becerra, J. Pat Cannady, Guy Dormer and Robin Walsh

Contents

Table S1 Calculated enthalpies (Hartrees) for several species by various different methods

Species	G3B3	G3MP2	G3Q	CBS-Q	CBS-QB3
SiH_2	-290.454684	-290.172922	-290.453102	-290.16017	-290.161403
2-butyne	-155.830293	-155.678744	-155.823469	-155.648155	-155.647968
2,3-dimethylsilirene	-446.367031	-446.933128	-446.359864	-445.894405	-445.892620

Table S2 .(see next page)

Table S3 Temperature dependent parameters used in RRKM calculations for 2,3-dimethylsilirane-d_2 decomposition

	T/K				
	296	368	430	523	612
TSa wavenumbers[a]/cm	41	46	49	54	56
	35	41	43	47	49
	35	40	42	46	48
	33	38	41	44	46
$Z_{LJ}(SF_6)/10^{-10}$ cm^3 molecule^{-1} s^{-1}	4.61	4.75	4.87	5.04	5.20

[a] Obtained by scaling SiD_2 and ring stretch modes (588, 513, 500, 484 cm^{-1}) by same factors as for 2,3-dimethylsilirene (paper, Table 7).

Table S2 Molecular and transition state parameters for RRKM calculations for 2,3-dimethylsilirene-d_2 decomposition at 612 K

	2,3-dimethylsilirene-d_2	TSa(d_2)
$\tilde{\nu}$ /cm^{-1}	2917(1)	2917(1)
	2914(3)	2914(3)
	2858(1)	2858(1)
	2855(1)	2855(1)
	1656(1)	1656(1)
	1524(1)	1524(1)
	1515(1)	1515(1)
	1455(1)	1455(1)
	1452(2)	1452(2)
	1451(1)	1451(1)
	1390(1)	1390(1)
	1386(1)	1386(1)
	1199(1)	1199(1)
	1065(1)	1065(1)
	1044(1)	1044(1)
	1040(1)	1040(1)
	1001(1)	1001(1)
	846(1)	715(1)
	715(1)	627(1)
	627(1)	326(1)
	588(1)	308(1)
	513(1)	205(1)
	500(1)	189(1)
	484(1)	116(1)
	326(1)	101(1)
	308(1)	56(1)
	205(1)	49(1)
	189(1)	48(1)
	116(1)	46(1)
	101(1)	
reaction coordinate/cm^{-1}	846	
path degeneracy	1	
E_o(critical energy)/kJ mol^{-1}	186.2	
Collision number (in SF_6) Z_{LJ}/10^{-10} cm^3 molecule^{-1} s^{-1}	5.20	

Note on Collision Numbers

Leonard-Jones collision numbers were calculated by the procedure recommended by Troe[S1]. The required parameters are shown in Table S3 below. Since no measurement is possible it was assumed that the LJ parameters for SiH_2 were the same as those for SiH_4[S2]. For $CH_3C{\equiv}CCH_3$, the parameters were estimated by comparison with those for related molecules[S2]. These lead to the value of 5.72×10^{-10} cm^3 molecule^{-1} s^{-1}. The calculated collision efficiency is shown, together with those for related reactions[S3], in Table S4.

References

S1. J. Troe, *J. Chem. Phys.*, 1977, **66**, 4758.

S2. R. C. Reid, J. M. Prausnitz and B. E. Poling, *The properties of Gases and Liquids*, 4th edn., McGraw-Hill, New York, 1988.

S3. R. Becerra and R. Walsh, *J. Organometallic Chem.*, 2001, **636**, 49.

Table S4 Some Lennard-Jones parameters

Molecule or reaction	σ/Å	(ε/k)K
SiH_2	4.08	207.6
$CH_3C{\equiv}CCH_3$	5.18	317
$SiH_2 + CH_3C{\equiv}CCH_3$	4.63	256.5

i

Table S5 Lennard-Jones collision efficiencies[b,c] at 298 K for some addition reactions of SiH_2

Substrate	k[a]	Z_{LJ}[a]	%Efficiency
C_2H_4[b]	3.5	4.92	71
C_3H_6[b]	3.4	5.31	64
C_2H_2[b]	4.0	4.90	82
$CH_3C{\equiv}CCH_3$[c]	4.3	5.72	75

[a] Units: 10^{-10} cm^3 molecule^{-1} s^{-1}. [b] Reference S3.
[c] This work

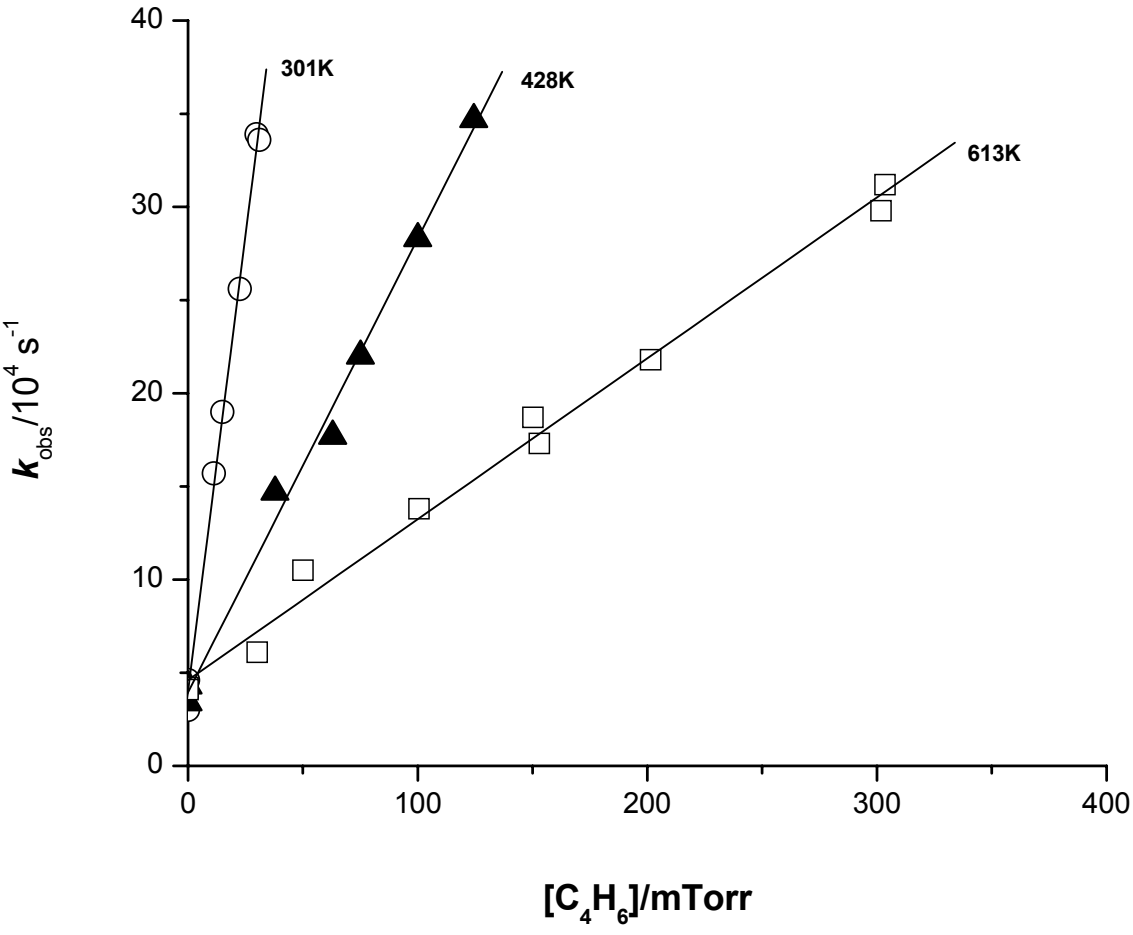

Fig. S1 Second order plots for reaction (H), SiH_2 + MeC≡CMe, at 10 Torr (He) at three temperatures (indicated).

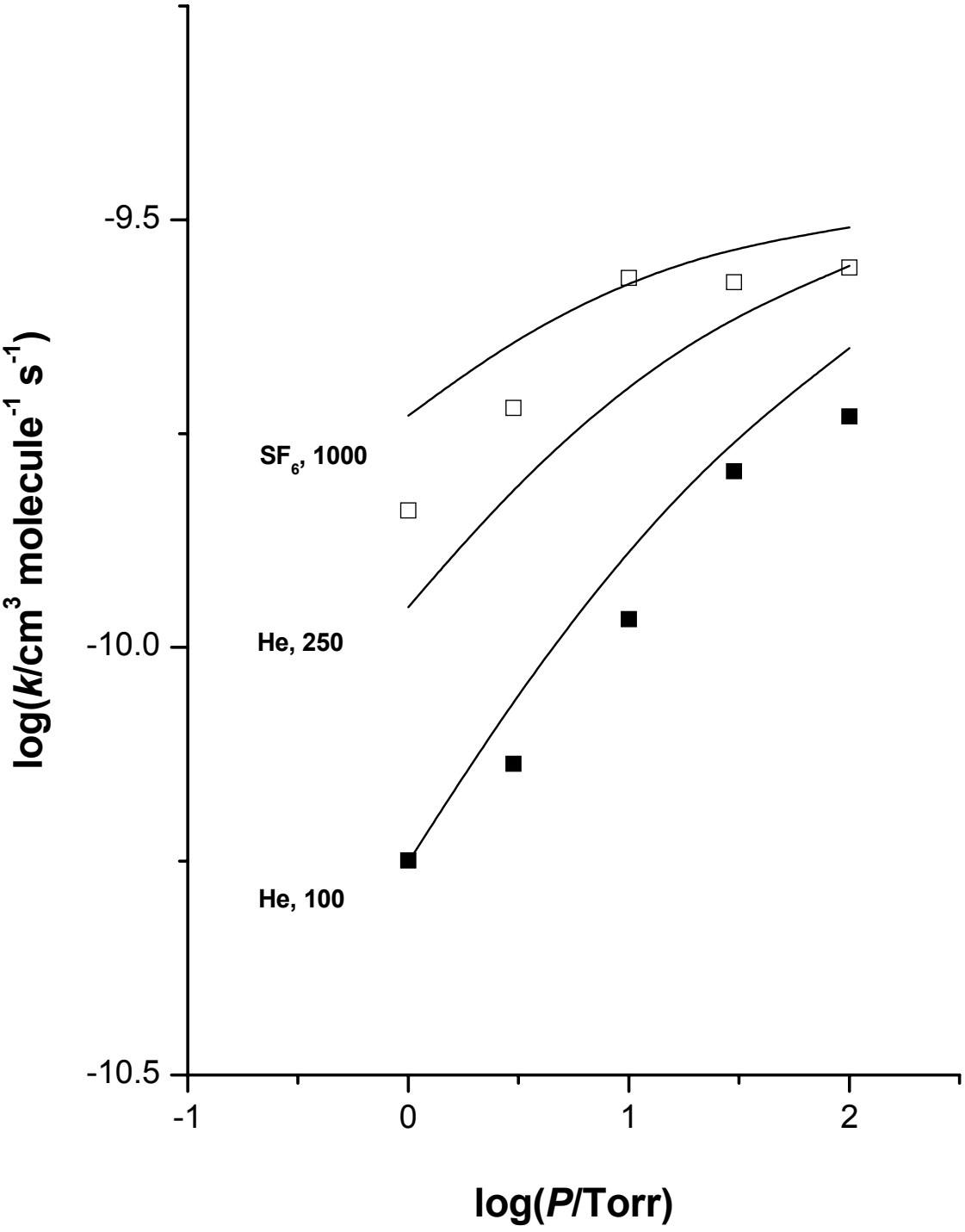

Fig. S2 Comparison of RRKM theoretical curves with experiment for pressure dependence of SiH_2 + MeC≡CMe $\rightarrow$ 2,3-dimethylsilirene in both He (filled symbols) and SF_6 (open symbols) at 429 K and several different energy removal parameters ($<\Delta E>_{down}$/cm^{-1}), as indicated.

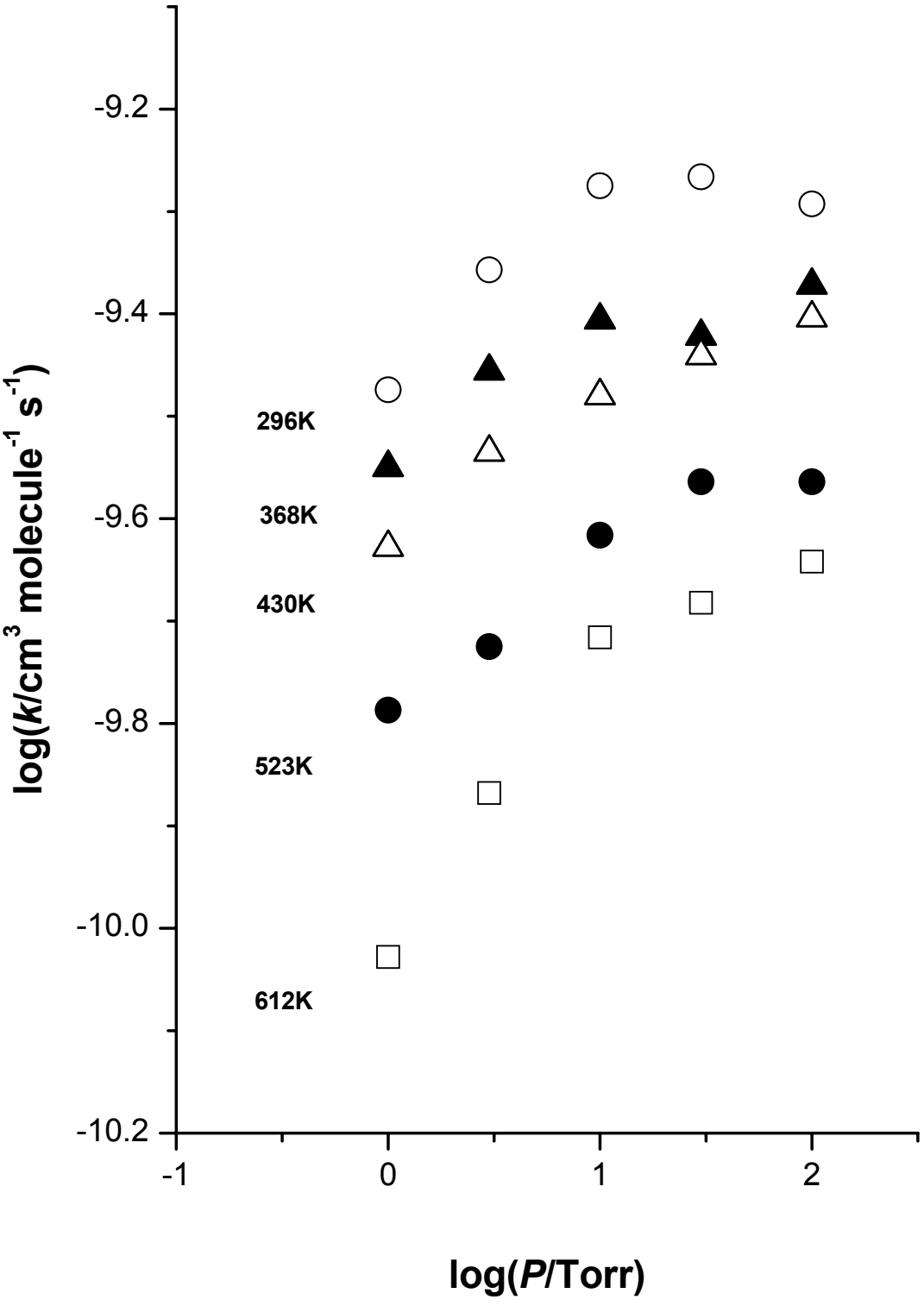

Fig. S3 Pressure dependence of second order rate constants for reaction (D), SiD_2 + MeC≡CMe, in the presence of SF_6 at five temperatures (indicated).