Supplementary Information

Time-resolved gas-phase kinetic studies of the reaction of dimethylsilylene with triethylsilane-1-d: kinetic isotope effect for the Si-H insertion process.

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Corrections to Gaussian output[1] for entropy

(a) *General*

1. Vibration wavenumber corrections made using formula[2]:

$$S_{\mathrm{vib}} = R[u/(e^{u}-1) - \ln(1-e^{-u})] \qquad \text{where } u = 1.4387(\omega/\mathrm{cm}^{-1})/(T/\mathrm{K})$$

2. Conversion of twisting vibrations into hindered internal rotations:

$S_{\mathrm{int\ rot}}$ obtained from Table 27-12 (ref 2, p.445) using values of partition function Q_{f} and internal rotation barrier V. Q_{f} is calculated from reduced internal rotation moment of inertia, I_{f}, using:

$$Q_{\mathrm{f}} = 0.360(I_{\mathrm{f}}/\mathrm{u\AA}^{2})^{1/2}(T/\mathrm{K})^{1/2}/\sigma$$

I_{f} is calculated from the Gaussian structure geometry for the molecular species.

(b) *Specifics for molecular species*[3]

1. Me_3SiH

Three Me-group twisting modes with adjusted wavenos, ω/cm^{-1}(G3) = 132, 147(2); ω/cm^{-1}(G3B3) = 139, 150, 160.

Three Me-group internal rotations with barriers, 1.84 kcal mol^{-1} [4], $\sigma = 3$ and I_{f} = 3.0 uÅ^2, Q_{f} (298K) = 3.6, V/RT = 3.1.

Entropy values (cal K^{-1} mol^{-1})	G3	G3B3
Gaussian entropy, Total	80.40	81.40
Vib	–15.84	–16.83
Waveno. Corrected Vib	+18.08	+17.62
Sub-total	82.62	82.19
Twisting mode contrib.	–8.33	–8.03
Internal Rotation contrib.	+8.31	+8.31
Symmetry contrib.	–2.18	–2.18
Corrected Total	80.42	80.29

2. $\underline{SiMe_2}$

Two Me-group twisting modes with adjusted wavenos, ω/cm^{-1}(G3)= 46, 98; ω/cm^{-1}(G3B3)= 92, 98.

Two Me-group internal rotations with barriers, 1.84 kJ mol^{-1} [4,5], σ = 3 and I_f = 3.0 uÅ^2, Q_f (298K) = 3.6, V/RT = 3.1.

Entropy values (cal K^{-1} mol^{-1})	G3	G3B3
Gaussian entropy, Total	73.28	72.92
Vib	–11.40	–11.01
Waveno. Corrected Vib	+12.68	+11.49
Sub-total	74.56	73.40
Twisting mode contrib.	–8.45	–7.11
Internal Rotation contrib.	+6.54	+6.54
Symmetry contrib.	–1.38	–1.38
Corrected Total	70.27	70.45

3. TS2

Five Me-group twisting modes with adjusted wavenos, ω/cm^{-1}(G3) = 129, 135(2), 146, 151; ω/cm^{-1}(G3B3) = 123, 132, 133, 139, 145.

Five Me-group internal rotations with barriers, 1.84 kcal mol^{-1} [4,5], σ = 3 and I_f = 3.0 uÅ^2, Q_f (298K) = 3.6, V/RT = 3.1.

Entropy values (cal K^{-1} mol^{-1})	G3	G3B3
Gaussian entropy, Total	109.03	111.88
Vib	–38.97	–41.81
Waveno. Corrected Vib	+43.41	+43.42
Sub-total	113.47	113.49
Twisting mode contrib.	–14.11	–14.44
Internal Rotation contrib.	+13.85	+13.85
Symmetry contrib.	0	0
Corrected Total	113.21	112.90

4. $Me_3SiSiMe_2H$

Five Me-group twisting modes with adjusted wavenos, ω/cm^{-1}(G3) = 142, 146, 148, 155, 156; ω/cm^{-1}(G3B3) = 151, 153, 154, 160, 161.

One Si–Si twisting mode with adjusted waveno, ω/cm^{-1}(G3) = 23; ω/cm^{-1}(G3B3) = 26.

Five Me-group internal rotations with barriers, 1.84 kcal mol^{-1} [4,5], σ = 3 and I_f = 3.0 uÅ^2, Q_f (298K) = 3.6, V/RT = 3.1.

One Si–Si internal rotation with barrier, 1.10 kcal mol^{-1} [6,7], σ = 3 and I_f = 3.0 uÅ^2, Q_f (298K) = 15.7, V/RT = 1.8.

Entropy values (cal K^{-1} mol^{-1})		G3	G3B3
Gaussian entropy,	Total	111.70	113.92
	Vib	–41.76	–43.96
Waveno. Corrected	Vib	+46.42	+45.65
	Sub-total	116.37	115.61
Twisting mode contrib.		–19.78	–19.12
Internal Rotation contrib.		+19.92	+19.92
Symmetry contrib.		0	0
Corrected	Total	116.51	116.41

References

1. M. J. Frisch et al, *Gaussian 03*, revision E.01, Gaussian, Inc., Wallingford CT, 2004. [For full reference see main paper, ref. 27.]
2. K. S. Pitzer and L. Brewer, *Thermodynamics*, 2nd Edn., McGraw-Hill, New York, 1961.
3. Energy units: calories; 1 cal = 4.184 J.
4. L. Pierce and D. H. Petersen, *J. Chem. Phys.*, 1960, **33**, 907.
5. Me group internal rotation barriers in species other than Me_3SiH are not known. We have assumed the same value as in Me_3SiH.
6. This barrier is not known. We have assumed the same value as for Si_2H_6[7].
7. J. R. Durig and J. S. Church, *J. Chem. Phys.*, 1980, **73**, 4784.