Supplementary Material (ESI) for *PCCP*

Supplementary Information

A Mechanistic Study of Cyclic Siloxane Pyrolyses at Low Pressures

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Table S1 Molecular and transition state parameters for RRKM calculation for dimethysiloxane decomposition at 983 K.

	dimethylsiloxane	TS1a	TS8
$\tilde{\nu}$ /cm^{-1}	2949(2)	2949(2)	3014(1)
	2905(1)	2905(1)	2965(1)
	2902(1)	2902(1)	2942(1)
	2852(1)	2852(1)	2915(1)
	2849(1)	2849(1)	2859(1)
	1433(1)	1433(1)	1729(1)
	1427(1)	1427(1)	1441(1)
	1421(1)	1421(1)	1420(1)
	1419(1)	1419(1)	1391(1)
	1299(1)	1299(1)	1265(1)
	1293(1)	1293(1)	1258(1)
	1211(1)	1211(1)	1224(1)
	840(1)	840(1)	871(1)
	788(1)	783(1)	840(1)
	783(1)	659(1)	787(1)
	675(1)	288(1)	738(1)
	659(1)	105(1)	701(1)
	590(1)	93(1)	568(1)
	288(1)	70(1)	406(1)
	256(1)	57(1)	321(1)
	206(1)	17(1)	259(1)
	62(1)	15(1)	250(1)
	15(1)		56(1)
reaction coordinate/cm^{-1}		590	659
path degeneracy		2	6
A factor/ s^{-1}		8.1×10^{16}	7.1×10^{12}
E_o(critical energy)/kJ mol^{-1}		347	339
Z_{LJ}/10^{-10} cm^3 molecule^{-1} s^{-1}	8.42[a]		

[a] Value calculated using the formulas recommended by Troe[1s].

Table S2 RRKM calculated values for k_{1a}[a] as a function of temperature and pressure

T/K	*P*/Torr			
	10^{-1}	10^{-2}	10^{-3}	10^{-4}
950	1.55×10^{-4}	4.51×10^{-5}	1.06×10^{-5}	2.05×10^{-6}
983	3.75×10^{-4}	1.57×10^{-4}	3.54×10^{-5}	6.70×10^{-6}
1000	1.07×10^{-3}	2.89×10^{-4}	6.38×10^{-5}	1.19×10^{-5}

[a] Units: s^{-1}

Table S3 Values for k_{4a}[a] estimated from ref 2s, assumed temperature independent in the range 950 – 1000 K

P/Torr			
10^{-1}	10^{-2}	10^{-3}	10^{-4}
6.3×10^{-13}	1.3×10^{-13}	2.0×10^{-14}	2.5×10^{-15}

[a] Units: cm^3 $molecule^{-1}$ s^{-1}

Table S4 Values for k_2[a] estimated from ref 3s[b]

Temp/K		
950	983	1000
1.62×10^{-14}	2.2×10^{-14}	2.5×10^{-14}

[a] Units: cm^3 $molecule^{-1}$ s^{-1}
[b] Assumed the same as for $CH_3 + (CH_3)_2CO$

References.

1s. J. Troe, *J. Chem. Phys.*, 1977, **66**, 4758.

2s. S. J. Klippenstein and L. B. Harding, *J. Phys. Chem. A*, 1999, **103**, 9388.

3s. S. H. Mousavipour and P. D. Pacey, *J. Phys. Chem.*, 1996, **100**, 3573. [Same as ref. 15 in paper].