Appendix

Molecular parameters used for SACM calculation and the master equation analysis.

Toluene (C_7H_8):
vibrational frequencies (in cm^{-1}): ν = 3085, 3070, 3058, 3037, 3028, 2979, 2950, 2920, 1604, 1584, 1493, 1455, 1455, 1455, 1378, 1331, 1313, 1208, 1176, 1153, 1080, 1040, 1040, 1028, 1002, 983, 973, 893, 841, 784, 734, 690, 620, 524, 467, 406, 347, 217 [1]
internal rotational constant (in cm^{-1}): 5.37 [2]
rotational constants (in cm^{-1}): A = 0.189, B = 0.084, C = 0.058 [3]
enthalpy of formation: Δ_fH^0(0 K) = 6119 cm^{-1} (73.2 kJ mol^{-1}) [4]
electronic partition function: Q_{el} = 1
Lennard-Jones parameter: $\sigma = 5.92 \times 10^{-10}$ m; ε/k_B = 410 K [5]

Benzyl (C_7H_7):
vibrational frequencies (in cm^{-1}): ν = 3060, 3060, 3050, 3040, 3030, 2930, 2860, 1600, 1550, 1480, 1440, 1440, 1350, 1330, 1300, 1270, 1160, 1160,1070, 1010, 980, 980, 950, 890, 820, 810, 750, 640, 610, 600, 520, 420, 360, 360, 290, 170 [6]
rotational constants (in cm^{-1}): A = 0.189, B = 0.0906, C = 0.0613 [6]
enthalpy of formation: Δ_fH^0(0 K) = 19142 cm^{-1} (229.0 kJ mol^{-1}) [7]
electronic partition function: Q_{el} = 2

Phenyl (C_6H_5):
vibrational frequencies (in cm^{-1}): ν = 3085, 3071, 3052, 3073, 3060, 1593, 1499, 1441, 1433, 1344, 1226, 1086, 1080, 1067, 1027, 1011, 976, 971, 966, 878, 813, 708, 629, 605, 586, 416, 400 [8]
rotational constants (in cm^{-1}): A = 0.209, B = 0.186, C = 0.098 [9]
enthalpy of formation: Δ_fH^0(0 K) = 29485 cm^{-1} (352.7 kJ mol^{-1}) [10]
electronic partition function: Q_{el} = 2

Methyl (CH_3):
vibrational frequencies (in cm^{-1}): ν = 3184, 3184, 3002, 1383, 1383, 580 [11]
rotational constants (in cm^{-1}): A = B = 9.578, C = 4.743 [12]
enthalpy of formation: Δ_fH^0(0 K) = 12514 cm^{-1} (149.7 kJ mol^{-1}) [13]
electronic partition function: Q_{el} = 2

H-atom:
enthalpy of formation: Δ_fH^0(0 K) = 18057 cm^{-1} (216.0 kJ mol^{-1}) [14]
electronic partition function: Q_{el} = 2

Ar:
Lennard-Jones parameter: $s = 3.47 \times 10^{-10}$ m; ε/k_B = 114 K. [15]

Benzyl + H	⇐	**Toluene**	⇒	**Phenyl + CH_3**
3060	⇐	3085	⇒	3071
3060	⇐	3070	⇒	3052
3050	⇐	3058	⇒	3085
3030	⇐	3037	⇒	3073
3040	⇐	3028	⇒	3184
reaction coordinate	⇐	2979	⇒	3184
2930	⇐	2950	⇒	3060
2860	⇐	2920	⇒	3002
1600	⇐	1604	⇒	1499
1550	⇐	1584	⇒	1593
1440	⇐	1455	⇒	1383
disappearing oscillator	⇐	1455	⇒	1383
1440	⇐	1455	⇒	reaction coordinate
1480	⇐	1493	⇒	1441
1330	⇐	1378	⇒	1433
1350	⇐	1331	⇒	1344
1300	⇐	1313	⇒	1226
1270	⇐	1208	⇒	1086
1160	⇐	1176	⇒	1080
1160	⇐	1153	⇒	1067
1070	⇐	1080	⇒	1027
600	⇐	1040	⇒	9.578 (methyl rotation)
disappearing oscillator	⇐	1040	⇒	9.578 (methyl rotation)
1010	⇐	1028	⇒	1011
980	⇐	1002	⇒	976
980	⇐	983	⇒	4.74 (methyl rotation)
950	⇐	973	⇒	707
890	⇐	893	⇒	878
820	⇐	841	⇒	840

810	⇐	784	⇒	708
750	⇐	734	⇒	971
640	⇐	690	⇒	629
610	⇐	620	⇒	605
520	⇐	524	⇒	586
420	⇐	467	⇒	416
360	⇐	406	⇒	348
360	⇐	347	⇒	580
170	⇐	217	⇒	0.209 (phenyl rotation)
290 (CH_2-vibration)	⇐	5.37 (internal rotation)	⇒	0.186 (phenyl rotation)
		0.084	⇒	0.098 (phenyl rotation)
0.0613 (external rotation)	⇐	0.189 (external rotation)		
Toluene treated as quasi-triatomic oblate symmetrical top				
Looseness Parameter: $a/b = 0.5$		Looseness Parameter: $a/b = 0.52$		
Morse Parameter: $b = 1.954\times10^{-10}$ m.		Morse Parameter: $b = 3.22\times10^{-10}$ m.		
Enthalpy of reaction: $\Delta_R H^0(0\ K) = 31080\ cm^{-1}$ (371.8 kJ mol^{-1})		Enthalpy of reaction: $\Delta_R H^0(0\ K) = 35880\ cm^{-1}$ (429.2 kJ mol^{-1})		

Table S1: Correlation schemes for vibrations and rotations used in the SACM calculations (all energies given in cm^{-1}).

References

[1] A.P. Hitchcock, J.D. Laposa, *J. Mol. Spec.*, 1975, **54**, 273.

[2] H.D. Rudolph, H. Dreizler, A. Jaeschke, P. Wendling, *Z. f. Naturforschung*, 1967, **22a**, 940.

[3] U. Brand, H. Hippler, L. Lindemann, J. Troe, *J. Phys. Chem.*, 1990, **94**, 6305.

[4] J. Chao, K.R. Hall, J.M. Yao, *Thermochim. Acta*, 1984, **72**, 323.

[5] F.M. Mourits, F.H.A. Rummers, *Can. J. Chem*, 1977, **55**, 3007.

[6] L.D. Brouwer, W. Müller-Markgraf, J. Troe, *J. Phys. Chem.*, 1988, **92**, 4905.

[7] H. Hippler, J. Troe, *J. Phys. Chem.*, 1994, **98**, 3903.

[8] J.G. Radziszewski, M.R. Nimlos, P.R. Winter, G.B. Ellison, *J. Am. Chem. Soc.*, 1996, **118**, 7400.

[9] J.G. Radziszewski, M.R. Nimlos, P.R. Winter, G.B. Ellison, *J. Am. Chem. Soc.*, 1996, **118**, 7400.

[10] G.E. Davico, V.M. Bierbaum, C.H. Depuy, G.B. Ellison, R.R. Squires, *J. Am. Chem. Soc.*, 1995, **117**, 2590-2599.

[11] M.W. Chase,Jr., C.A. Davies, J.R. Downey, D.J. Frurip, R.A. McDonald, A.N. Syverud, *J. Phys. Chem. Ref. Data*, 1985, **14**, Supplement No.1.

[12] G. Herzberg, in *Molecular Spectra and Molecular Structure I-III*, second edition, Krieger, Malabar, 1989.

[13] L.V. Gurvich, I.V. Veyts, C.B. Alcock, in *Thermodynamic Properties of Individual Substances*, 4th edition, Vol. 1 and 2, Hemisphere Publishing Corporation, New York, Washington, Philadelphia, London, 1991.

[14] M.W. Chase,Jr., C.A. Davies, J.R. Downey, D.J. Frurip, R.A. McDonald, A.N. Syverud, *J. Phys. Chem. Ref. Data*, 1985, **14**, Supplement No.1.

[15] F.M. Mourits, F.H.A. Rummers, *Can. J. Chem*, 1977, **55**, 3007.