Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Catalysis and tunnelling in the unimolecular decay of Criegee intermediates

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1 Anharmonic Partition Functions

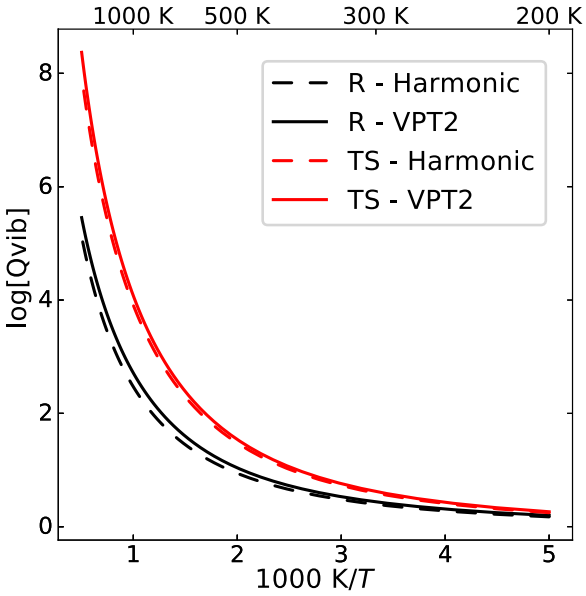

Figure S1: Comparison of Harmonic and VPT2 vibrational partition functions for the unmethylated reactant and transition state (with water)

2 Rate data

The table below lists the calculated rate constants used in this work. Units are s^{-1} for unimolecular reactions, and $cm^3 molecule^{-1} s^{-1}$ for bimolecular reactions. The reactions are:

- a - Unmethylated, Uncatalysed - 1D-SCTST
- b - Unmethylated, Uncatalysed - FD-SCTST (MP2 x matrix)
- c - Unmethylated, Uncatalysed - FD-SCTST (B3LYP x matrix)
- d - Methylated, Uncatalysed - 1D-SCTST
- e - Methylated, Uncatalysed - FD-SCTST (MP2 x matrix)
- f - Unmethylated, catalysed - 1D-SCTST (TS1)
- g - Unmethylated, catalysed - 1D-SCTST (TS2)
- h - Unmethylated, catalysed - FD-SCTST (TS1, MP2 x matrix)
- i - Unmethylated, catalysed - FD-SCTST (TS1, B3LYP x matrix)
- j - Unmethylated, catalysed - 1D-SCTST (TS1, FD value of x_{FF})

T (K)	a	b	c	d	e	f	g	h	i	j
200	5.49E-01	1.10E+00	1.05E+00	1.40E+00	3.42E+00	1.20E-19	1.11E-19	1.49E-18	1.78E-18	5.46E-19
223	2.09E+00	3.56E+00	3.33E+00	5.48E+00	1.12E+01	1.82E-19	1.65E-19	1.50E-18	1.71E-18	6.12E-19
245	8.32E+00	1.22E+01	1.11E+01	2.24E+01	3.88E+01	2.82E-19	2.53E-19	1.60E-18	1.73E-18	7.33E-19
268	3.40E+01	4.31E+01	3.87E+01	9.27E+01	1.40E+02	4.44E-19	3.93E-19	1.80E-18	1.84E-18	9.29E-19
291	1.37E+02	1.55E+02	1.36E+02	3.73E+02	5.08E+02	6.98E-19	6.12E-19	2.14E-18	2.05E-18	1.23E-18
313	5.22E+02	5.41E+02	4.69E+02	1.40E+03	1.78E+03	1.09E-18	9.48E-19	2.64E-18	2.39E-18	1.68E-18
336	1.84E+03	1.79E+03	1.53E+03	4.84E+03	5.85E+03	1.66E-18	1.45E-18	3.36E-18	2.90E-18	2.33E-18
359	5.91E+03	5.51E+03	4.68E+03	1.52E+04	1.78E+04	2.49E-18	2.17E-18	4.37E-18	3.62E-18	3.25E-18
381	1.73E+04	1.56E+04	1.32E+04	4.33E+04	4.95E+04	3.66E-18	3.19E-18	5.74E-18	4.60E-18	4.52E-18
404	4.63E+04	4.06E+04	3.43E+04	1.13E+05	1.27E+05	5.25E-18	4.59E-18	7.55E-18	5.93E-18	6.24E-18
427	1.14E+05	9.80E+04	8.27E+04	2.72E+05	3.01E+05	7.38E-18	6.47E-18	9.90E-18	7.68E-18	8.51E-18
449	2.61E+05	2.20E+05	1.86E+05	6.07E+05	6.65E+05	1.02E-17	8.94E-18	1.29E-17	9.96E-18	1.14E-17
472	5.58E+05	4.62E+05	3.93E+05	1.27E+06	1.38E+06	1.38E-17	1.21E-17	1.67E-17	1.29E-17	1.52E-17
495	1.12E+06	9.16E+05	7.82E+05	2.50E+06	2.69E+06	1.83E-17	1.62E-17	2.14E-17	1.66E-17	1.99E-17
517	2.14E+06	1.72E+06	1.48E+06	4.68E+06	4.98E+06	2.39E-17	2.13E-17	2.71E-17	2.12E-17	2.58E-17
540	3.87E+06	3.08E+06	2.67E+06	8.35E+06	8.81E+06	3.09E-17	2.76E-17	3.40E-17	2.69E-17	3.30E-17
563	6.73E+06	5.28E+06	4.62E+06	1.43E+07	1.49E+07	3.93E-17	3.53E-17	4.23E-17	3.40E-17	4.17E-17
585	1.12E+07	8.72E+06	7.70E+06	2.35E+07	2.43E+07	4.95E-17	4.46E-17	5.22E-17	4.26E-17	5.21E-17
608	1.81E+07	1.39E+07	1.24E+07	3.75E+07	3.83E+07	6.16E-17	5.57E-17	6.37E-17	5.30E-17	6.45E-17
631	2.83E+07	2.14E+07	1.94E+07	5.79E+07	5.85E+07	7.59E-17	6.89E-17	7.72E-17	6.55E-17	7.91E-17
653	4.30E+07	3.22E+07	2.95E+07	8.70E+07	8.69E+07	9.27E-17	8.44E-17	9.28E-17	8.05E-17	9.62E-17
676	6.37E+07	4.71E+07	4.36E+07	1.27E+08	1.26E+08	1.12E-16	1.02E-16	1.11E-16	9.83E-17	1.16E-16
698	9.20E+07	6.73E+07	6.32E+07	1.82E+08	1.78E+08	1.35E-16	1.23E-16	1.31E-16	1.19E-16	1.39E-16
721	1.30E+08	9.41E+07	8.95E+07	2.56E+08	2.46E+08	1.60E-16	1.48E-16	1.55E-16	1.44E-16	1.65E-16
744	1.80E+08	1.29E+08	1.25E+08	3.52E+08	3.33E+08	1.90E-16	1.75E-16	1.81E-16	1.73E-16	1.95E-16
766	2.45E+08	1.74E+08	1.70E+08	4.76E+08	4.43E+08	2.23E-16	2.07E-16	2.11E-16	2.07E-16	2.29E-16
789	3.28E+08	2.31E+08	2.29E+08	6.33E+08	5.81E+08	2.61E-16	2.42E-16	2.44E-16	2.46E-16	2.67E-16
812	4.33E+08	3.01E+08	3.03E+08	8.30E+08	7.50E+08	3.04E-16	2.83E-16	2.82E-16	2.91E-16	3.10E-16
834	5.63E+08	3.88E+08	3.95E+08	1.07E+09	9.54E+08	3.52E-16	3.28E-16	3.24E-16	3.43E-16	3.59E-16
857	7.22E+08	4.94E+08	5.10E+08	1.37E+09	1.20E+09	4.05E-16	3.78E-16	3.70E-16	4.03E-16	4.13E-16
880	9.15E+08	6.21E+08	6.50E+08	1.73E+09	1.49E+09	4.64E-16	4.35E-16	4.22E-16	4.72E-16	4.72E-16
902	1.15E+09	7.73E+08	8.19E+08	2.16E+09	1.83E+09	5.30E-16	4.97E-16	4.79E-16	5.49E-16	5.39E-16

T (K)	a	b	c	d	e	f	g	h	i	j
925	1.42E+09	9.51E+08	1.02E+09	2.67E+09	2.22E+09	6.03E-16	5.67E-16	5.42E-16	6.38E-16	6.12E-16
948	1.75E+09	1.16E+09	1.26E+09	3.27E+09	2.67E+09	6.82E-16	6.43E-16	6.11E-16	7.38E-16	6.92E-16
970	2.13E+09	1.40E+09	1.55E+09	3.96E+09	3.18E+09	7.70E-16	7.27E-16	6.87E-16	8.51E-16	7.81E-16
993	2.57E+09	1.68E+09	1.88E+09	4.77E+09	3.76E+09	8.66E-16	8.20E-16	7.71E-16	9.77E-16	8.78E-16
1016	3.07E+09	2.01E+09	2.26E+09	5.70E+09	4.42E+09	9.71E-16	9.21E-16	8.62E-16	1.12E-15	9.83E-16
1038	3.65E+09	2.37E+09	2.71E+09	6.75E+09	5.15E+09	1.09E-15	1.03E-15	9.62E-16	1.28E-15	1.10E-15
1061	4.31E+09	2.79E+09	3.22E+09	7.95E+09	5.95E+09	1.21E-15	1.15E-15	1.07E-15	1.45E-15	1.22E-15
1084	5.05E+09	3.25E+09	3.80E+09	9.31E+09	6.85E+09	1.35E-15	1.28E-15	1.19E-15	1.65E-15	1.36E-15
1106	5.89E+09	3.77E+09	4.45E+09	1.08E+10	7.82E+09	1.49E-15	1.42E-15	1.32E-15	1.87E-15	1.51E-15
1129	6.82E+09	4.36E+09	5.19E+09	1.25E+10	8.89E+09	1.65E-15	1.58E-15	1.46E-15	2.11E-15	1.66E-15
1152	7.86E+09	5.00E+09	6.03E+09	1.44E+10	1.01E+10	1.82E-15	1.74E-15	1.61E-15	2.37E-15	1.84E-15
1174	9.00E+09	5.72E+09	6.96E+09	1.65E+10	1.13E+10	2.00E-15	1.92E-15	1.77E-15	2.66E-15	2.02E-15
1197	1.03E+10	6.51E+09	7.99E+09	1.88E+10	1.27E+10	2.20E-15	2.11E-15	1.95E-15	2.98E-15	2.22E-15
1220	1.17E+10	7.37E+09	9.14E+09	2.13E+10	1.41E+10	2.41E-15	2.32E-15	2.14E-15	3.33E-15	2.43E-15
1242	1.32E+10	8.32E+09	1.04E+10	2.41E+10	1.57E+10	2.64E-15	2.54E-15	2.34E-15	3.71E-15	2.66E-15
1265	1.48E+10	9.35E+09	1.18E+10	2.71E+10	1.73E+10	2.88E-15	2.77E-15	2.56E-15	4.12E-15	2.90E-15
1288	1.66E+10	1.05E+10	1.33E+10	3.03E+10	1.91E+10	3.13E-15	3.03E-15	2.80E-15	4.57E-15	3.16E-15
1310	1.86E+10	1.17E+10	1.50E+10	3.39E+10	2.10E+10	3.41E-15	3.29E-15	3.06E-15	5.06E-15	3.43E-15
1333	2.06E+10	1.30E+10	1.68E+10	3.77E+10	2.30E+10	3.70E-15	3.58E-15	3.33E-15	5.59E-15	3.73E-15
1356	2.29E+10	1.44E+10	1.88E+10	4.18E+10	2.51E+10	4.01E-15	3.89E-15	3.63E-15	6.15E-15	4.04E-15
1378	2.53E+10	1.59E+10	2.09E+10	4.62E+10	2.72E+10	4.34E-15	4.21E-15	3.95E-15	6.77E-15	4.37E-15
1401	2.79E+10	1.76E+10	2.32E+10	5.09E+10	2.95E+10	4.69E-15	4.56E-15	4.28E-15	7.43E-15	4.72E-15
1424	3.06E+10	1.93E+10	2.57E+10	5.59E+10	3.20E+10	5.06E-15	4.92E-15	4.65E-15	8.13E-15	5.09E-15
1446	3.36E+10	2.12E+10	2.84E+10	6.13E+10	3.45E+10	5.46E-15	5.31E-15	5.03E-15	8.89E-15	5.49E-15
1469	3.67E+10	2.32E+10	3.12E+10	6.70E+10	3.71E+10	5.87E-15	5.72E-15	5.45E-15	9.71E-15	5.90E-15
1492	4.00E+10	2.53E+10	3.43E+10	7.30E+10	3.98E+10	6.31E-15	6.15E-15	5.89E-15	1.06E-14	6.34E-15
1514	4.35E+10	2.76E+10	3.76E+10	7.94E+10	4.27E+10	6.77E-15	6.60E-15	6.36E-15	1.15E-14	6.80E-15
1537	4.71E+10	3.00E+10	4.11E+10	8.62E+10	4.56E+10	7.25E-15	7.08E-15	6.87E-15	1.25E-14	7.29E-15
1559	5.10E+10	3.25E+10	4.48E+10	9.33E+10	4.86E+10	7.77E-15	7.59E-15	7.41E-15	1.35E-14	7.80E-15
1582	5.51E+10	3.52E+10	4.88E+10	1.01E+11	5.18E+10	8.30E-15	8.12E-15	7.98E-15	1.46E-14	8.34E-15
1605	5.93E+10	3.81E+10	5.30E+10	1.09E+11	5.50E+10	8.87E-15	8.68E-15	8.59E-15	1.58E-14	8.91E-15
1627	6.38E+10	4.10E+10	5.74E+10	1.17E+11	5.84E+10	9.46E-15	9.27E-15	9.24E-15	1.71E-14	9.50E-15
1650	6.85E+10	4.42E+10	6.21E+10	1.26E+11	6.18E+10	1.01E-14	9.89E-15	9.93E-15	1.84E-14	1.01E-14
1673	7.34E+10	4.75E+10	6.71E+10	1.35E+11	6.54E+10	1.07E-14	1.05E-14	1.07E-14	1.98E-14	1.08E-14
1695	7.85E+10	5.10E+10	7.23E+10	1.44E+11	6.90E+10	1.14E-14	1.12E-14	1.14E-14	2.13E-14	1.15E-14
1718	8.38E+10	5.46E+10	7.78E+10	1.54E+11	7.27E+10	1.21E-14	1.19E-14	1.23E-14	2.28E-14	1.22E-14
1741	8.93E+10	5.85E+10	8.36E+10	1.64E+11	7.65E+10	1.29E-14	1.27E-14	1.31E-14	2.44E-14	1.29E-14
1763	9.50E+10	6.25E+10	8.96E+10	1.75E+11	8.04E+10	1.37E-14	1.34E-14	1.41E-14	2.62E-14	1.37E-14
1786	1.01E+11	6.67E+10	9.60E+10	1.86E+11	8.44E+10	1.45E-14	1.42E-14	1.51E-14	2.80E-14	1.45E-14
1809	1.07E+11	7.10E+10	1.03E+11	1.98E+11	8.85E+10	1.53E-14	1.51E-14	1.61E-14	2.98E-14	1.54E-14
1831	1.14E+11	7.56E+10	1.10E+11	2.10E+11	9.26E+10	1.62E-14	1.60E-14	1.72E-14	3.18E-14	1.62E-14
1854	1.20E+11	8.04E+10	1.17E+11	2.22E+11	9.69E+10	1.71E-14	1.69E-14	1.84E-14	3.39E-14	1.72E-14
1877	1.27E+11	8.53E+10	1.25E+11	2.35E+11	1.01E+11	1.81E-14	1.78E-14	1.96E-14	3.61E-14	1.81E-14
1899	1.34E+11	9.05E+10	1.32E+11	2.49E+11	1.06E+11	1.91E-14	1.88E-14	2.09E-14	3.83E-14	1.91E-14
1922	1.41E+11	9.59E+10	1.41E+11	2.62E+11	1.10E+11	2.01E-14	1.99E-14	2.23E-14	4.07E-14	2.02E-14
1945	1.49E+11	1.01E+11	1.49E+11	2.77E+11	1.15E+11	2.12E-14	2.10E-14	2.38E-14	4.31E-14	2.12E-14
1967	1.56E+11	1.07E+11	1.58E+11	2.91E+11	1.19E+11	2.23E-14	2.21E-14	2.53E-14	4.57E-14	2.24E-14
1990	1.64E+11	1.13E+11	1.68E+11	3.06E+11	1.24E+11	2.35E-14	2.32E-14	2.69E-14	4.84E-14	2.35E-14

3 Structure Data

This following are structures optimised at MP2/aug-cc-pVTZ level using the 'tight' convergence criterion in Gaussian 09. Values in Angstroms.

Reactant(R = H)			
C	-0.70495700	0.42531000	-1.40808300
H	-1.36654400	0.36962900	-2.25971700
O	-0.26856900	1.61111900	-1.20725800
O	0.55038900	1.78959900	-0.18747200
C	-0.29006100	-0.66095700	-0.52184900
H	-0.55254900	-0.39629400	0.50689400
H	-0.73840000	-1.60417000	-0.81452400
H	0.80251600	-0.72033300	-0.52465100

Reactant (R=Me)			
C	-0.76775945	0.46311872	-1.38988232
O	-0.52315719	1.64849879	-0.99826027
O	0.28354144	1.78558430	0.07153032
C	-0.16199578	-0.65576620	-0.65841883
H	-0.45382943	-0.58184378	0.39260970
H	-0.44570400	-1.61123230	-1.08816235
H	0.92284732	-0.52020158	-0.65322394
C	-1.65830272	0.34435775	-2.56889507
H	-1.96580106	1.32722105	-2.91583188
H	-1.14146494	-0.18230657	-3.37246936
H	-2.53939984	-0.24472004	-2.31027418

TS (R = H)			
C	-0.73292006	0.31840102	-1.42870711
H	-1.32666910	0.27135102	-2.33135618
O	-0.56233405	1.53871012	-1.00734308
O	0.01843700	1.51141711	0.23998302
C	-0.35571303	-0.69337005	-0.53732504
H	-0.44980503	0.18935201	0.41501703
H	-0.81143206	-1.66134213	-0.69056005
H	0.70334506	-0.73072706	-0.28244902

TS (R = Me)			
C	-0.72275205	0.30781202	-1.46220011
O	-0.27868902	1.49973911	-1.17244709
O	0.30280602	1.49457711	0.08624701
C	-0.53554904	-0.65276005	-0.45192603
H	-0.40752503	0.32997602	0.39097203
H	-1.19040209	-1.51277311	-0.48840804
H	0.50173804	-0.89100507	-0.21830502
C	-1.53408712	0.23751202	-2.70106221
H	-1.02919108	-0.37421203	-3.44777626
H	-2.48707919	-0.24014702	-2.47423519
H	-1.71087413	1.23277409	-3.10172124

Ts (R = H, with water) - Structure 1			
O	-0.26667290	1.10237511	0.07148587
C	-0.79889370	-0.04368055	-0.16930577
O	1.04445640	1.25166643	-0.44163574
C	-0.17288403	-1.11350749	-0.81438209
H	-0.79457849	-1.98181743	-0.97344732
H	0.49070605	-0.82446327	-1.62551200
H	0.80553953	-1.23257981	0.02919242
O	1.95598480	-0.74205543	0.56923895

H	1.66370194	0.27355302	0.18605957
H	2.01880744	-0.73437670	1.53202959
H	-1.76789855	-0.11179868	0.31580985

Ts (R= H, with water) - Structure 2			
O	0.27126534	1.10842984	-0.06496641
C	0.79508730	-0.04263140	0.16885825
O	-1.04297497	1.25608767	0.44190040
C	0.16681493	-1.10481263	0.82593025
H	0.78509919	-1.97708978	0.97732565
H	-0.46806349	-0.79950369	1.65354248
H	-0.82492263	-1.21998339	-0.00891109
O	-1.85342045	-0.70080561	-0.72435831
H	-1.64065413	0.28793583	-0.22335777
H	-2.72095967	-1.01118030	-0.43852353
H	1.75940560	-0.11882128	-0.32381104

Ts (R=Me, with water) - Structure 1			
O	-0.25254081	1.09649379	0.07447085
C	-0.81513243	-0.04458076	-0.15968241
O	1.06473103	1.22639937	-0.44446274
C	-0.17124690	-1.10213733	-0.81813010
H	-0.78539286	-1.97434447	-0.99163809
H	0.48294756	-0.79382670	-1.62913338
H	0.79892161	-1.23023851	0.02656244
O	1.95063474	-0.75407585	0.58311497
H	1.64518594	0.29088773	0.17127750
H	2.00956346	-0.74798601	1.54580050
C	-2.15668977	-0.14960196	0.47912287
H	-2.35915720	0.71621232	1.10276642
H	-2.91591692	-0.23021282	-0.29823286
H	-2.19944571	-1.05821318	1.07834411

Ts (R=Me, with water) - Structure 2			
O	0.26212800	1.10432636	-0.04938349
C	0.81294222	-0.04492808	0.17085450
O	-1.06044379	1.23051841	0.45826483
C	0.16331687	-1.09712828	0.83489181
H	0.77253222	-1.97525753	0.99661532
H	-0.46147163	-0.77610593	1.66363425
H	-0.81680435	-1.21466439	-0.00332044
O	-1.83499760	-0.70120725	-0.74714623
H	-1.61763070	0.31096548	-0.20012436
C	2.14397527	-0.16398618	-0.48545800
H	2.36868489	0.72343406	-1.06965598
H	2.90895108	-0.31415915	0.27527009
H	2.14134902	-1.04047094	-1.13272513
H	-2.70600027	-1.02207397	-0.48570616

Product (R = H)			
C	0.17162307	-1.79737047	0.02444877
H	0.76343379	-2.69600127	-0.03778792
H	-0.90102545	-1.86851647	0.11916949
C	0.78101880	-0.61671569	-0.05744899
H	1.84973060	-0.46950863	-0.13115632
O	0.03942435	0.53408604	-0.12219700
O	0.86202891	1.58916502	0.46058076
H	0.79848327	2.23856523	-0.25516178

Product (R=Me)			
C	0.18643354	-1.76160325	0.01674387
H	0.71977904	-2.69796619	-0.02982396
H	-0.88875763	-1.76341550	0.11080400
C	0.85352430	-0.60931022	-0.09132815
O	0.07534824	0.52452037	-0.23303551
O	0.67343417	1.58655695	0.58286059
H	0.71903093	2.27954102	-0.09181728
C	2.33143829	-0.44541973	-0.19291307
H	2.58943078	0.12513078	-1.08547923
H	2.72358942	0.08694087	0.67043285
H	2.80152585	-1.42435716	-0.24746521

Water			
O	-1.39251812	-0.76581701	0.00000000
H	-0.43207200	-0.72409591	0.00000000
H	-1.67379621	0.15346926	0.00000000