

Supplementary Materials

Table S1. The calculated energies and Gibbs energies relative to R1/R3/R5 + O₂ at M06-2X and ROCBS-QB3 levels (all in kJ/mol)^(a) and *T*₁-Diagnostics at ROCCSD/6-31+G(d') level

Species	M06-2X		ROCBS-QB3		T_1 -Diag
	$\Delta_r E_{0K}$	$\Delta_r G_{298K}$	$\Delta_r E_{0K}$	$\Delta_r G_{298K}$	
R1 + O₂					
R1-2OO- <i>anti</i>	-39.9	7.9	-39.4	8.5	0.02076
R1-2OO- <i>syn</i>	-44.2	4.3	-42.1	6.4	0.02109
R1-6OO- <i>anti</i>	-42.0	5.5	-37.9	9.6	0.02074
R1-6OO- <i>syn</i>	-47.5	-0.7	-42.5	4.4	0.02110
TS (R1 + O ₂ → R1-2OO- <i>anti</i>)	8.6	54.4	-8.2	37.7	0.03393
TS (R1 + O ₂ → R1-2OO- <i>syn</i>)	9.8	56.3	-11.2	35.3	0.03522
TS (R1 + O ₂ → R1-6OO- <i>anti</i>)	22.6	68.1	-1.5	44.0	0.03401
TS (R1 + O ₂ → R1-6OO- <i>syn</i>)	14.5	59.6	-5.8	39.3	0.03564
R1-26OO- <i>anti</i>	-75.3	-24.3	-91.9	-41.0	0.02084
R1-26OO- <i>syn</i>	-84.2	-34.1	-102.3	-52.2	0.02089
R1-24OO- <i>syn</i>	-15.5	36.4			
R1-46OO- <i>syn</i>	-12.7	38.0			
TS (R1-2OO- <i>anti</i> → R1-26OO- <i>anti</i>)	25.1	76.2	8.0	59.1	0.02649
TS (R1-2OO- <i>syn</i> → R1-26OO- <i>syn</i>)	8.4	59.9	-10.0	41.6	0.02772
TS (R1-6OO- <i>anti</i> → R1-26OO- <i>anti</i>)	24.7	75.6	10.1	61.0	0.02707
TS (R1-6OO- <i>syn</i> → R1-26OO- <i>syn</i>)	7.5	57.4	-8.8	41.1	0.02831
TS (R1-2OO- <i>syn</i> → R1-24OO- <i>syn</i>)	87.7	139.0			
TS (R1-6OO- <i>syn</i> → R1-46OO- <i>syn</i>)	91.4	141.3			
R1-2O-56O- <i>syn</i>	-169.7	-118.9	-158.6	-107.8	0.01687
R1-6O-23O- <i>syn</i>	-177.4	-128.4	-165.9	-116.9	0.01681
TS (R1-26OO- <i>syn</i> → R1-2O-56O- <i>syn</i>)	31.8	81.8	-24.3	25.7	0.04471
TS (R1-26OO- <i>syn</i> → R1-6O-23O- <i>syn</i>)	28.2	77.6	-26.9	22.5	0.04387
R3 + O₂					
R3-2OO- <i>anti</i>	-47.4	1.9	-47.0	2.3	0.02056
R3-2OO- <i>syn</i>	-50.1	-0.3	-46.9	2.9	0.01986
R3-4OO- <i>anti</i>	-42.2	4.6	-42.8	4.0	0.02056
R3-4OO- <i>syn</i>	-41.3	7.9	-39.2	10.0	0.01990
2,3,6-TMP + HO ₂	-120.0	-119.6	-113.2	-112.7	
TS (R3 + O ₂ → R3-2OO- <i>anti</i>)	11.3	58.1	-11.8	35.0	0.03407
TS (R3 + O ₂ → R3-2OO- <i>syn</i>)	9.4	56.8	-9.8	37.6	0.03499
TS (R3 + O ₂ → R3-4OO- <i>anti</i>)	14.8	59.2	-9.6	34.8	0.03370
TS (R3 + O ₂ → R3-4OO- <i>syn</i>)	15.5	61.0	-5.1	40.4	0.03478
TS (R3 + O ₂ → 2,3,6-TMP + HO ₂)	25.7	70.2	8.0	52.5	0.05292
R3-24OO- <i>anti</i>	-88.0	-34.1	-106.6	-52.7	0.01913
R3-24OO- <i>syn</i>	-92.6	-38.8	-111.3	-57.5	0.01904
R3-26OO- <i>syn</i>	-16.6	35.0			
R3-46OO- <i>syn</i>	-6.5	43.7			
TS (R3-2OO- <i>anti</i> → R3-24OO- <i>anti</i>)	11.2	65.3	-7.6	46.5	0.02766

TS (R3-200- <i>syn</i> → R3-2400- <i>syn</i>)	−2.3	51.9	−19.5	34.7	0.02850
TS (R3-400- <i>anti</i> → R3-2400- <i>anti</i>)	17.2	69.5	−2.8	49.4	0.02739
TS (R3-400- <i>syn</i> → R3-2400- <i>syn</i>)	3.4	56.1	−14.1	38.6	0.02800
TS (R3-200- <i>syn</i> → R3-2600- <i>syn</i>)	82.0	135.0			
TS (R3-400- <i>syn</i> → R3-4600- <i>syn</i>)	102.4	153.9			
R3-20-450- <i>syn</i>	−176.7	−123.8	−167.4	−114.5	0.01676
R3-40-120- <i>syn</i>	−177.9	−126.0	−171.4	−119.5	0.01667
TS (R3-2400- <i>syn</i> → R3-20-450- <i>syn</i>)	23.3	77.9	−33.3	21.3	0.04745
TS (R3-2400- <i>syn</i> → R3-40-120- <i>syn</i>)	21.0	74.9	−34.3	19.6	0.04685

R5 + O₂

R5-400- <i>anti</i>	−40.8	10.4	−41.2	10.0	0.02053
R5-400- <i>syn</i>	−44.6	6.8	−42.7	8.6	0.01974
R5-600- <i>anti</i>	−40.4	7.1	−39.3	8.1	0.02056
R5-600- <i>syn</i>	−39.0	10.5	−35.8	13.7	0.01992
2,4,5-TMP + HO ₂	−116.8	−113.6	−110.7	−107.5	
TS (R5 + O ₂ → R5-400- <i>anti</i>)	14.5	64.3	−9.7	40.1	0.03367
TS (R5 + O ₂ → R5-400- <i>syn</i>)	12.1	62.1	−8.6	41.5	0.03474
TS (R5 + O ₂ → R5-600- <i>anti</i>)	23.1	70.7	−1.5	46.1	0.03334
TS (R5 + O ₂ → R5-600- <i>syn</i>)	20.0	69.4	−0.5	48.8	0.03454
TS (R5 + O ₂ → 2,4,5-TMP + HO ₂)	23.6	68.6	5.1	50.2	0.04072
R5-4600- <i>anti</i>	−74.5	−21.3	−91.1	−37.9	0.02116
R5-4600- <i>syn</i>	−83.1	−29.7	−100.2	−46.7	0.02080
R5-2400- <i>syn</i>	−13.4	42.0			
R5-2600- <i>syn</i>	−14.4	39.8			
TS (R5-400- <i>anti</i> → R5-4600- <i>anti</i>)	25.6	80.8	5.5	59.9	0.02711
TS (R5-400- <i>syn</i> → R5-4600- <i>syn</i>)	8.0	63.1	−10.5	44.6	0.02774
TS (R5-600- <i>anti</i> → R5-4600- <i>anti</i>)	26.4	79.4	1.1	54.1	0.02801
TS (R5-600- <i>syn</i> → R5-4600- <i>syn</i>)	10.7	64.3	−5.1	48.5	0.02883
TS (R5-400- <i>syn</i> → R5-2400- <i>syn</i>)	93.6	148.2			
TS (R5-600- <i>syn</i> → R5-2600- <i>syn</i>)	85.5	138.7			
R5-40-160- <i>syn</i>	−170.9	−116.5	−162.0	−107.7	0.01660
R5-60-340- <i>syn</i>	−173.3	−122.5	−162.7	−111.9	0.01673
TS (R5-4600- <i>syn</i> → R5-40-160- <i>syn</i>)	29.5	84.2	−24.5	30.3	0.04708
TS (R5-4600- <i>syn</i> → R5-60-340- <i>syn</i>)	31.0	84.5	−25.7	27.7	0.04840

(a) All based on M06-2X geometries and vibrational frequencies; M06-2X = M06-2X/6-311++G(2df,2p).

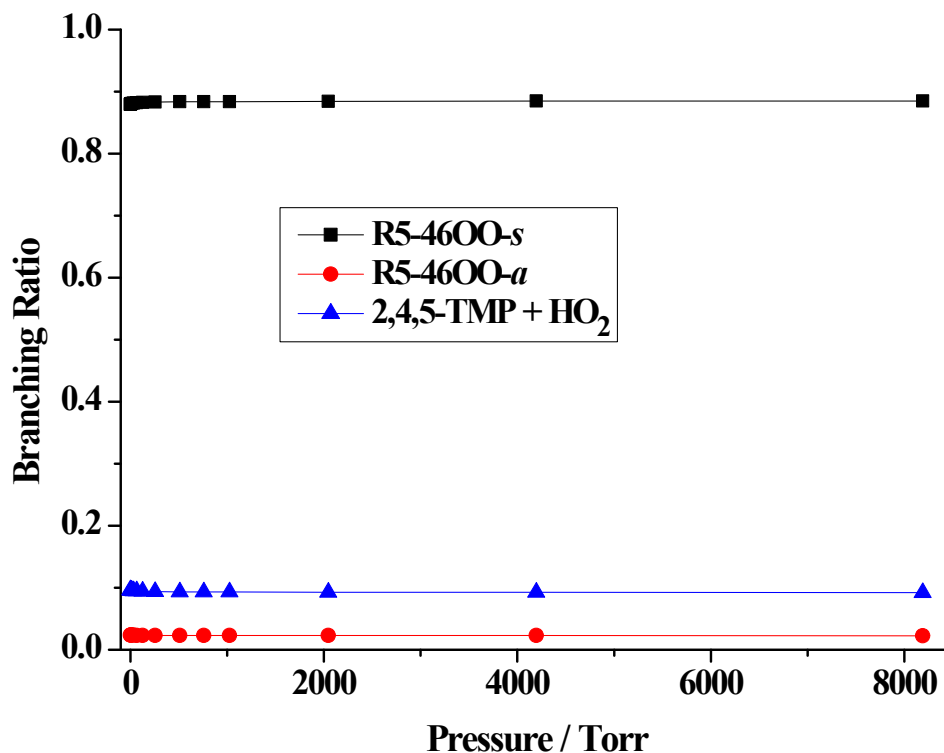


Figure S1. Pressure-Dependent Yields of R5-46OO-s, R5-46OO-a, and 2,4,5-TMP + HO₂ From RRKM-ME Calculations for Reaction of R5 and O₂ at 298 K

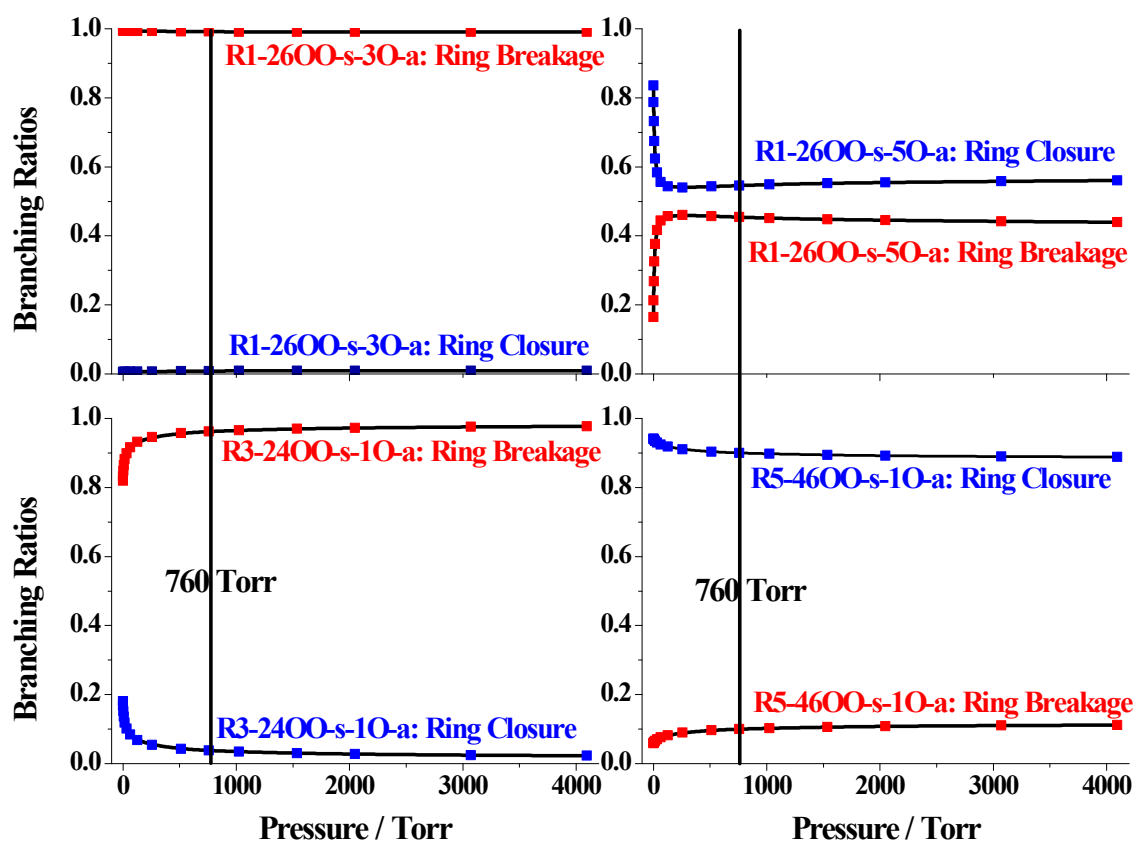


Figure S2. Pressure-Dependent Branching Ratios of Ring-Closure and Ring-Breakage Channels from RRKM-ME Calculations for The Bicyclic Alkoxy Radicals R1-26OO-s-3O-a, R1-26OO-s-5O-a, R3-24OO-s-1O-a, and R5-46OO-a-1O-a at 298 K