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

Theoretical Study of the Oxidation Mechanisms of Naphthalene Initiated by Hydroxyl Radicals: The O_2 Addition Reaction Pathways

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Electronic Supplementary Information (ESI)

Table S1: Effective rate constants (in cm^3 $molecule^{-1}$ s^{-1}) for the reported reaction channels obtained by means of RRKM theory at different pressures and temperatures, according to the computed UM06-2x/aug-cc-pVTZ energy profiles (x=1,3 and y=2,4).

Table S1*a*: [T= 298 K; *syn* isomer]

Reaction / Pressure	IMx→R1+O_2 k_{-1} (s^{-1})	IM1→R1-2OO-s k_2(**1**) (s^{-1})	IM3→R1-4OO-s k_2(**3**) (s^{-1})	k_{eff}(**1**) R1+O_2⇌R1-2OO-s (cm^3 $molecule^{-1}$ s^{-1})	k_{eff}(**3**) R1+O_2⇌R1-4OO-s (cm^3 $molecule^{-1}$ s^{-1})
1.00E+04	4.36E+16	1.78E+05	1.07E+06	3.93E-19	2.38E-18
1.00E+02	4.36E+16	1.78E+05	1.07E+06	3.93E-19	2.38E-18
1.00E+00	4.36E+16	1.77E+05	1.07E+06	3.93E-19	2.36E-18
1.00E-02	4.36E+16	1.54E+05	7.55E+05	3.41E-19	1.67E-18
1.00E-04	4.36E+16	2.82E+04	6.65E+04	6.23E-20	1.47E-19
1.00E-06	4.36E+16	7.09E+02	1.12E+03	1.57E-21	2.49E-21
1.00E-08	4.36E+16	8.02E+00	1.17E+01	1.78E-23	2.58E-23
1.00E-10	4.36E+16	8.04E-02	1.17E-01	1.78E-25	2.59E-25
1.00E-12	4.36E+16	8.04E-04	1.17E-03	1.78E-27	2.59E-27

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Table S1*b*: [T= 336 K; *syn* isomer]

Reaction / Pressure	IMx→R1+O_2 k_{-1} (s^{-1})	IM1→R1-2OO-*s* k_2(**1**) (s^{-1})	IM3→R1-4OO-*s* k_2(**3**) (s^{-1})	k_{eff}(**1**) R1+O_2⇌R1-2OO-*s* (cm^3 $molecule^{-1}$ s^{-1})	k_{eff}(**3**) R1+O_2⇌R1-4OO-*s* (cm^3 $molecule^{-1}$ s^{-1})
1.00E+04	1.80E+16	7.11E+05	3.57E+06	1.05E-18	5.29E-18
1.00E+02	1.80E+16	7.11E+05	3.57E+06	1.05E-18	5.29E-18
1.00E+00	1.80E+16	7.08E+05	3.53E+06	1.05E-18	5.23E-18
1.00E-02	1.80E+16	5.49E+05	2.03E+06	8.13E-19	3.01E-18
1.00E-04	1.80E+16	6.23E+04	1.12E+05	9.23E-20	1.67E-19
1.00E-06	1.80E+16	1.19E+03	1.59E+03	1.76E-21	2.35E-21
1.00E-08	1.80E+16	1.29E+01	1.62E+01	1.91E-23	2.41E-23
1.00E-10	1.80E+16	1.29E-01	1.62E-01	1.91E-25	2.41E-25
1.00E-12	1.80E+16	1.29E-03	1.62E-03	1.91E-27	2.41E-27

Table S1*c*: [T= 400 K; *syn* isomer]

Reaction / Pressure	IMx→R1+O_2 k_{-1} (s^{-1})	IM1→R1-2OO-*s* k_2(**1**) (s^{-1})	IM3→R1-4OO-*s* k_2(**3**) (s^{-1})	k_{eff}(**1**) R1+O_2⇌R1-2OO-*s* (cm^3 $molecule^{-1}$ s^{-1})	k_{eff}(**3**) R1+O_2⇌R1-4OO-*s* (cm^3 $molecule^{-1}$ s^{-1})
1.00E+04	6.11E+15	4.00E+06	1.59E+07	3.69E-18	1.47E-17
1.00E+02	6.11E+15	4.00E+06	1.59E+07	3.69E-18	1.47E-17
1.00E+00	6.11E+15	3.96E+06	1.55E+07	3.65E-18	1.43E-17
1.00E-02	6.11E+15	2.31E+06	5.74E+06	2.13E-18	5.29E-18
1.00E-04	6.11E+15	1.25E+05	1.67E+05	1.15E-19	1.54E-19
1.00E-06	6.11E+15	1.73E+03	1.95E+03	1.60E-21	1.79E-21
1.00E-08	6.11E+15	1.79E+01	1.96E+01	1.65E-23	1.81E-23
1.00E-10	6.11E+15	1.79E-01	1.96E-01	1.65E-25	1.81E-25
1.00E-12	6.11E+15	1.79E-03	1.96E-03	1.65E-27	1.81E-27

Table S1*d*: [T= 298 K; *anti* isomer]

Reaction / Pressure	IMy→R1+O_2 k_{-1} (s^{-1})	IM2→R1-2OO-*a* k_2(**2**) (s^{-1})	IM4→R1-4OO-*a* k_2(**4**) (s^{-1})	k_{eff}(**2**) R1+O_2⇌R1-2OO-*a* (cm^3 $molecule^{-1}$ s^{-1})	k_{eff}(**4**) R1+O_2⇌R1-4OO-*a* (cm^3 $molecule^{-1}$ s^{-1})
1.00E+04	1.88E+19	1.18E+06	9.39E+06	4.92E-21	3.90E-20
1.00E+02	1.88E+19	1.18E+06	9.38E+06	4.92E-21	3.90E-20
1.00E+00	1.88E+19	1.17E+06	8.92E+06	4.85E-21	3.71E-20
1.00E-02	1.88E+19	6.54E+05	2.82E+06	2.72E-21	1.17E-20
1.00E-04	1.88E+19	4.44E+04	9.44E+04	1.85E-22	3.92E-22
1.00E-06	1.88E+19	7.47E+02	1.19E+03	3.11E-24	4.95E-24
1.00E-08	1.88E+19	7.83E+00	1.20E+01	3.26E-26	4.99E-26
1.00E-10	1.88E+19	7.84E-02	1.20E-01	3.26E-28	4.99E-28
1.00E-12	1.88E+19	7.84E-04	1.20E-03	3.26E-30	4.99E-30

Table S1*e*: [T= 336 K; *anti* isomer]

Reaction / Pressure	IMy→R1+O_2 k_{-1} (s^{-1})	IM2→R1-2OO-*a* k_2(**2**) (s^{-1})	IM4→R1-4OO-*a* k_2(**4**) (s^{-1})	k_{eff}(**2**) R1+O_2⇌R1-2OO-*a* (cm^3 $molecule^{-1}$ s^{-1})	k_{eff}(**4**) R1+O_2⇌R1-4OO-*a* (cm^3 $molecule^{-1}$ s^{-1})
1.00E+04	3.92E+18	5.00E+06	3.19E+07	2.45E-20	1.56E-19
1.00E+02	3.92E+18	4.99E+06	3.18E+07	2.45E-20	1.56E-19
1.00E+00	3.92E+18	4.85E+06	2.90E+07	2.37E-20	1.42E-19
1.00E-02	3.92E+18	2.00E+06	6.01E+06	9.79E-21	2.94E-20
1.00E-04	3.92E+18	8.70E+04	1.42E+05	4.26E-22	6.97E-22
1.00E-06	3.92E+18	1.23E+03	1.64E+03	6.04E-24	8.05E-24
1.00E-08	3.92E+18	1.27E+01	1.65E+01	6.21E-26	8.09E-26
1.00E-10	3.92E+18	1.27E-01	1.65E-01	6.21E-28	8.09E-28
1.00E-12	3.92E+18	1.27E-03	1.65E-03	6.21E-30	8.09E-30

Table S1*f*: [T= 400 K; *anti* isomer]

Reaction / Pressure	IMy→R1+O_2 k_{-1} (s^{-1})	IM2→R1-2OO-*a* k_2(**2**) (s^{-1})	IM4→R1-4OO-*a* k_2(**4**) (s^{-1})	k_{eff}(**2**) R1+O_2⇌R1-2OO-*a* (cm^3 $molecule^{-1}$ s^{-1})	k_{eff}(**4**) R1+O_2⇌R1-4OO-*a* (cm^3 $molecule^{-1}$ s^{-1})
1.00E+04	5.61E+17	3.01E+07	1.46E+08	1.87E-19	9.10E-19
1.00E+02	5.61E+17	3.01E+07	1.46E+08	1.87E-19	9.08E-19
1.00E+00	5.61E+17	2.77E+07	1.17E+08	1.72E-19	7.29E-19
1.00E-02	5.61E+17	6.23E+06	1.19E+07	3.87E-20	7.40E-20
1.00E-04	5.61E+17	1.50E+05	1.86E+05	9.32E-22	1.16E-21
1.00E-06	5.61E+17	1.76E+03	1.97E+03	1.09E-23	1.22E-23
1.00E-08	5.61E+17	1.78E+01	1.97E+01	1.11E-25	1.23E-25
1.00E-10	5.61E+17	1.78E-01	1.97E-01	1.11E-27	1.23E-27
1.00E-12	5.61E+17	1.78E-03	1.97E-03	1.11E-29	1.23E-29

Table S2: Kinetic rate constants (in s^{-1}), effective rate constants, and branching ratios for all reaction steps involved in the reported chemical pathways at ambient temperature and different pressures using the RRKM theory, according to the computed UM06-2x/aug-cc-pVTZ energy profiles (z=1,2,3,4).

Table S2*a*:

Parameter / Reaction pathway	$P = 10^4$ bar				
	Rate constant			effective rate constant k_{eff} (cm^3 $molecule^{-1}$ s^{-1})	Branching ratio (R)
	K_p	k_{-1} IMz →R1+O_2	k_2 IMz→R2	R1+O_2⇌R2	
***T*=298 K**					
R1+O_2⇌R1-2OO-*syn*	5.38E-05	4.36E+16	1.78E+05	3.93E-19	13.95
R1+O_2⇌R1-4OO-*syn*	5.38E-05	4.36E+16	1.07E+06	2.38E-18	84.49
R1+O_2⇌R1-2OO-*anti*	1.01E-07	1.88E+19	1.18E+06	4.92E-21	0.17
R1+O_2⇌R1-4OO-*anti*	1.01E-07	1.88E+19	9.39E+06	3.90E-20	1.38
***T*=336 K**					
R1+O_2⇌R1-2OO-*syn*	3.60E-05	4.36E+16	7.11E+05	1.05E-18	16.10
R1+O_2⇌R1-4OO-*syn*	3.60E-05	4.36E+16	3.57E+06	5.29E-18	81.13
R1+O_2⇌R1-2OO-*anti*	1.19E-07	1.88E+19	5.00E+06	2.45E-20	0.38
R1+O_2⇌R1-4OO-*anti*	1.19E-07	1.88E+19	3.19E+07	1.56E-19	2.39
***T*=400 K**					
R1+O_2⇌R1-2OO-*syn*	2.24E-05	4.36E+16	4.00E+06	3.69E-18	18.94
R1+O_2⇌R1-4OO-*syn*	2.24E-05	4.36E+16	1.59E+07	1.47E-17	75.43
R1+O_2⇌R1-2OO-*anti*	1.51E-07	1.88E+19	3.01E+07	1.87E-19	0.96
R1+O_2⇌R1-4OO-*anti*	1.51E-07	1.88E+19	1.46E+08	9.10E-19	4.67

Table S2*b*:

Parameter / Reaction pathway	$P = 10^2$ bar				
	Rate constant			effective rate constant k_{eff} (cm^3 $molecule^{-1}$ s^{-1})	Branching ratio (R)
	K_p	k_{-1} IMz →R1+O_2	k_2 IMz→R2	R1+O_2⇌R2	
***T*=298 K**					
R1+O_2⇌R1-2OO-*syn*	5.38E-05	4.36E+16	1.78E+05	3.93E-19	13.95
R1+O_2⇌R1-4OO-*syn*	5.38E-05	4.36E+16	1.07E+06	2.38E-18	84.49
R1+O_2⇌R1-2OO-*anti*	1.01E-07	1.88E+19	1.18E+06	4.92E-21	0.17
R1+O_2⇌R1-4OO-*anti*	1.01E-07	1.88E+19	9.38E+06	3.90E-20	1.38
***T*=336 K**					
R1+O_2⇌R1-2OO-*syn*	3.60E-05	4.36E+16	7.11E+05	1.05E-18	16.10
R1+O_2⇌R1-4OO-*syn*	3.60E-05	4.36E+16	3.57E+06	5.29E-18	81.13
R1+O_2⇌R1-2OO-*anti*	1.19E-07	1.88E+19	4.99E+06	2.45E-20	0.38
R1+O_2⇌R1-4OO-*anti*	1.19E-07	1.88E+19	3.18E+07	1.56E-19	2.39
***T*=400 K**					
R1+O_2⇌R1-2OO-*syn*	2.24E-05	4.36E+16	4.00E+06	3.69E-18	18.94
R1+O_2⇌R1-4OO-*syn*	2.24E-05	4.36E+16	1.59E+07	1.47E-17	75.44
R1+O_2⇌R1-2OO-*anti*	1.51E-07	1.88E+19	3.01E+07	1.87E-19	0.96
R1+O_2⇌R1-4OO-*anti*	1.51E-07	1.88E+19	1.46E+08	9.08E-19	4.66

Table S2*c*:

Parameter / Reaction pathway	P = 1.0 bar				
	Rate constant			effective rate constant k_{eff}(cm^3 molecule^{-1} s^{-1})	Branching ratio (R)
	K_p	k_{-1} IMz →R1+O_2	k_2 IMz→R2	R1+O_2⇌R2	
***T*=298 K**					
R1+O_2⇌R1-2OO-*syn*	5.38E-05	4.36E+16	1.77E+05	3.93E-19	14.06
R1+O_2⇌R1-4OO-*syn*	5.38E-05	4.36E+16	1.07E+06	2.36E-18	84.44
R1+O_2⇌R1-2OO-*anti*	1.01E-07	1.88E+19	1.17E+06	4.85E-21	0.17
R1+O_2⇌R1-4OO-*anti*	1.01E-07	1.88E+19	8.92E+06	3.71E-20	1.33
***T*=336 K**					
R1+O_2⇌R1-2OO-*syn*	3.60E-05	4.36E+16	7.08E+05	1.05E-18	16.29
R1+O_2⇌R1-4OO-*syn*	3.60E-05	4.36E+16	3.53E+06	5.23E-18	81.14
R1+O_2⇌R1-2OO-*anti*	1.19E-07	1.88E+19	4.85E+06	2.37E-20	0.37
R1+O_2⇌R1-4OO-*anti*	1.19E-07	1.88E+19	2.90E+07	1.42E-19	2.20
***T*=400 K**					
R1+O_2⇌R1-2OO-*syn*	2.24E-05	4.36E+16	3.96E+06	3.65E-18	19.36
R1+O_2⇌R1-4OO-*syn*	2.24E-05	4.36E+16	1.55E+07	1.43E-17	75.86
R1+O_2⇌R1-2OO-*anti*	1.51E-07	1.88E+19	2.77E+07	1.72E-19	0.91
R1+O_2⇌R1-4OO-*anti*	1.51E-07	1.88E+19	1.17E+08	7.29E-19	3.87

Table S2*d*:

Parameter / Reaction pathway	P = 10^{-2} bar				
	Rate constant			effective rate constant k_{eff}(cm^3 molecule^{-1} s^{-1})	Branching ratio (R)
	K_p	k_{-1} IMz →R1+O_2	k_2 IMz→R2	R1+O_2⇌R2	
***T*=298 K**					
R1+O_2⇌R1-2OO-*syn*	5.38E-05	4.36E+16	1.54E+05	3.41E-19	16.84
R1+O_2⇌R1-4OO-*syn*	5.38E-05	4.36E+16	7.55E+05	1.67E-18	82.45
R1+O_2⇌R1-2OO-*anti*	1.01E-07	1.88E+19	6.54E+05	2.72E-21	0.13
R1+O_2⇌R1-4OO-*anti*	1.01E-07	1.88E+19	2.82E+06	1.17E-20	0.58
***T*=336 K**					
R1+O_2⇌R1-2OO-*syn*	3.60E-05	4.36E+16	5.49E+05	8.13E-19	21.05
R1+O_2⇌R1-4OO-*syn*	3.60E-05	4.36E+16	2.03E+06	3.01E-18	77.94
R1+O_2⇌R1-2OO-*anti*	1.19E-07	1.88E+19	2.00E+06	9.79E-21	0.25
R1+O_2⇌R1-4OO-*anti*	1.19E-07	1.88E+19	6.01E+06	2.94E-20	0.76
***T*=400 K**					
R1+O_2⇌R1-2OO-*syn*	2.24E-05	4.36E+16	2.31E+06	2.13E-18	28.28
R1+O_2⇌R1-4OO-*syn*	2.24E-05	4.36E+16	5.74E+06	5.29E-18	70.23
R1+O_2⇌R1-2OO-*anti*	1.51E-07	1.88E+19	6.23E+06	3.87E-20	0.51
R1+O_2⇌R1-4OO-*anti*	1.51E-07	1.88E+19	1.19E+07	7.40E-20	0.98

Table S2*e*:

Parameter / Reaction pathway	$P = 10^{-4}$ bar				
	Rate constant			effective rate constant k_{eff}(cm^3 molecule^{-1} s^{-1})	Branching ratio (R)
	K_p	k_{-1} IMz →R1+O_2	k_2 IMz→R2	R1+O_2⇌R2	
***T*=298 K**					
R1+O_2⇌R1-2OO-*syn*	5.38E-05	4.36E+16	2.82E+04	6.23E-20	29.68
R1+O_2⇌R1-4OO-*syn*	5.38E-05	4.36E+16	6.65E+04	1.47E-19	70.04
R1+O_2⇌R1-2OO-*anti*	1.01E-07	1.88E+19	4.44E+04	1.85E-22	0.09
R1+O_2⇌R1-4OO-*anti*	1.01E-07	1.88E+19	9.44E+04	3.92E-22	0.19
***T*=336 K**					
R1+O_2⇌R1-2OO-*syn*	3.60E-05	4.36E+16	6.23E+04	9.23E-20	35.44
R1+O_2⇌R1-4OO-*syn*	3.60E-05	4.36E+16	1.12E+05	1.67E-19	64.13
R1+O_2⇌R1-2OO-*anti*	1.19E-07	1.88E+19	8.70E+04	4.26E-22	0.16
R1+O_2⇌R1-4OO-*anti*	1.19E-07	1.88E+19	1.42E+05	6.97E-22	0.27
***T*=400 K**					
R1+O_2⇌R1-2OO-*syn*	2.24E-05	4.36E+16	1.25E+05	1.15E-19	42.42
R1+O_2⇌R1-4OO-*syn*	2.24E-05	4.36E+16	1.67E+05	1.54E-19	56.81
R1+O_2⇌R1-2OO-*anti*	1.51E-07	1.88E+19	1.50E+05	9.32E-22	0.34
R1+O_2⇌R1-4OO-*anti*	1.51E-07	1.88E+19	1.86E+05	1.16E-21	0.43

Table S2*f*:

Parameter / Reaction pathway	$P = 10^{-6}$ bar				
	Rate constant			effective rate constant k_{eff}(cm^3 molecule^{-1} s^{-1})	Branching ratio (R)
	K_p	k_{-1} IMz →R1+O_2	k_2 IMz→R2	R1+O_2⇌R2	
***T*=298 K**					
R1+O_2⇌R1-2OO-*syn*	5.38E-05	4.36E+16	7.09E+02	1.57E-21	38.59
R1+O_2⇌R1-4OO-*syn*	5.38E-05	4.36E+16	1.12E+03	2.49E-21	61.21
R1+O_2⇌R1-2OO-*anti*	1.01E-07	1.88E+19	7.47E+02	3.11E-24	0.08
R1+O_2⇌R1-4OO-*anti*	1.01E-07	1.88E+19	1.19E+03	4.95E-24	0.12
***T*=336 K**					
R1+O_2⇌R1-2OO-*syn*	3.60E-05	4.36E+16	1.19E+03	1.76E-21	42.68
R1+O_2⇌R1-4OO-*syn*	3.60E-05	4.36E+16	1.59E+03	2.35E-21	56.98
R1+O_2⇌R1-2OO-*anti*	1.19E-07	1.88E+19	1.23E+03	6.04E-24	0.15
R1+O_2⇌R1-4OO-*anti*	1.19E-07	1.88E+19	1.64E+03	8.05E-24	0.20
***T*=400 K**					
R1+O_2⇌R1-2OO-*syn*	2.24E-05	4.36E+16	1.73E+03	1.60E-21	46.88
R1+O_2⇌R1-4OO-*syn*	2.24E-05	4.36E+16	1.95E+03	1.79E-21	52.44
R1+O_2⇌R1-2OO-*anti*	1.51E-07	1.88E+19	1.76E+03	1.09E-23	0.32
R1+O_2⇌R1-4OO-*anti*	1.51E-07	1.88E+19	1.97E+03	1.22E-23	0.36

Table S2*g*:

Parameter / Reaction pathway	$P = 10^{-8}$ bar				
	Rate constant			effective rate constant k_{eff}(cm^3 molecule^{-1} s^{-1})	Branching ratio (R)
	K_p	k_{-1} IMz →R1+O_2	k_2 IMz→R2	R1+O_2⇌R2	
***T*=298 K**					
R1+O_2⇌R1-2OO-*syn*	5.38E-05	4.36E+16	8.02E+00	1.78E-23	40.75
R1+O_2⇌R1-4OO-*syn*	5.38E-05	4.36E+16	1.17E+01	2.58E-23	59.06
R1+O_2⇌R1-2OO-*anti*	1.01E-07	1.88E+19	7.83E+00	3.26E-26	0.07
R1+O_2⇌R1-4OO-*anti*	1.01E-07	1.88E+19	1.20E+01	4.99E-26	0.11
***T*=336 K**					
R1+O_2⇌R1-2OO-*syn*	3.60E-05	4.36E+16	1.29E+01	1.91E-23	44.07
R1+O_2⇌R1-4OO-*syn*	3.60E-05	4.36E+16	1.62E+01	2.41E-23	55.60
R1+O_2⇌R1-2OO-*anti*	1.19E-07	1.88E+19	1.27E+01	6.21E-26	0.14
R1+O_2⇌R1-4OO-*anti*	1.19E-07	1.88E+19	1.65E+01	8.09E-26	0.19
***T*=400 K**					
R1+O_2⇌R1-2OO-*syn*	2.24E-05	4.36E+16	1.79E+01	1.65E-23	47.37
R1+O_2⇌R1-4OO-*syn*	2.24E-05	4.36E+16	1.96E+01	1.81E-23	51.96
R1+O_2⇌R1-2OO-*anti*	1.51E-07	1.88E+19	1.78E+01	1.11E-25	0.32
R1+O_2⇌R1-4OO-*anti*	1.51E-07	1.88E+19	1.97E+01	1.23E-25	0.35

Table S2*h*:

Parameter / Reaction pathway	$P = 10^{-10}$ bar				
	Rate constant			effective rate constant k_{eff}(cm^3 molecule^{-1} s^{-1})	Branching ratio (R)
	K_p	k_{-1} IMz →R1+O_2	k_2 IMz→R2	R1+O_2⇌R2	
***T*=298 K**					
R1+O_2⇌R1-2OO-*syn*	5.38E-05	4.36E+16	8.04E-02	1.78E-25	40.66
R1+O_2⇌R1-4OO-*syn*	5.38E-05	4.36E+16	1.17E-01	2.59E-25	59.16
R1+O_2⇌R1-2OO-*anti*	1.01E-07	1.88E+19	7.84E-02	3.26E-28	0.07
R1+O_2⇌R1-4OO-*anti*	1.01E-07	1.88E+19	1.20E-01	4.99E-28	0.11
***T*=336 K**					
R1+O_2⇌R1-2OO-*syn*	3.60E-05	4.36E+16	1.29E-01	1.91E-25	44.07
R1+O_2⇌R1-4OO-*syn*	3.60E-05	4.36E+16	1.62E-01	2.41E-25	55.60
R1+O_2⇌R1-2OO-*anti*	1.19E-07	1.88E+19	1.27E-01	6.21E-28	0.14
R1+O_2⇌R1-4OO-*anti*	1.19E-07	1.88E+19	1.65E-01	8.09E-28	0.19
***T*=400 K**					
R1+O_2⇌R1-2OO-*syn*	2.24E-05	4.36E+16	1.79E-01	1.65E-25	47.37
R1+O_2⇌R1-4OO-*syn*	2.24E-05	4.36E+16	1.96E-01	1.81E-25	51.96
R1+O_2⇌R1-2OO-*anti*	1.51E-07	1.88E+19	1.78E-01	1.11E-27	0.32
R1+O_2⇌R1-4OO-*anti*	1.51E-07	1.88E+19	1.97E-01	1.23E-27	0.35

Table S2*i*:

Parameter / Reaction pathway	$P = 10^{-12}$ bar				
	Rate constant			effective rate constant k_{eff}(cm^3 molecule^{-1} s^{-1})	Branching ratio (R)
	K_p	k_{-1} IMz →R1+O_2	k_2 IMz→R2	R1+O_2⇌R2	
***T*=298 K**					
R1+O_2⇌R1-2OO-*syn*	5.38E-05	4.36E+16	8.04E-04	1.78E-27	40.66
R1+O_2⇌R1-4OO-*syn*	5.38E-05	4.36E+16	1.17E-03	2.59E-27	59.16
R1+O_2⇌R1-2OO-*anti*	1.01E-07	1.88E+19	7.84E-04	3.26E-30	0.07
R1+O_2⇌R1-4OO-*anti*	1.01E-07	1.88E+19	1.20E-03	4.99E-30	0.11
***T*=336 K**					
R1+O_2⇌R1-2OO-*syn*	3.60E-05	4.36E+16	1.29E-03	1.91E-27	44.07
R1+O_2⇌R1-4OO-*syn*	3.60E-05	4.36E+16	1.62E-03	2.41E-27	55.60
R1+O_2⇌R1-2OO-*anti*	1.19E-07	1.88E+19	1.27E-03	6.21E-30	0.14
R1+O_2⇌R1-4OO-*anti*	1.19E-07	1.88E+19	1.65E-03	8.09E-30	0.19
***T*=400 K**					
R1+O_2⇌R1-2OO-*syn*	2.24E-05	4.36E+16	1.79E-03	1.65E-27	47.37
R1+O_2⇌R1-4OO-*syn*	2.24E-05	4.36E+16	1.96E-03	1.81E-27	51.96
R1+O_2⇌R1-2OO-*anti*	1.51E-07	1.88E+19	1.78E-03	1.11E-29	0.32
R1+O_2⇌R1-4OO-*anti*	1.51E-07	1.88E+19	1.97E-03	1.23E-29	0.35

Table S3: Dependence upon the pressure and temperature of the regioselectivities [RSI =R(**3**)–R(**1**)/R(**1**)+R(**3**)] and [RSI= R(**4**)–R(**2**)/R(**2**)+R(**4**)] of O_2 addition in *syn* and *anti* modes onto the naphthalene-OH adduct $[C_{10}H_8OH]^{\bullet}$, according to the RRKM estimates of effective rate constants [k_{eff}(**1**), k_{eff}(**2**), k_{eff}(**3**), k_{eff}(**4**)].

Table S3*a*: (T= 298 K; *syn* isomer)

P (bar)	k_{eff}(**1**)	k_{eff}(**3**)	k_{eff}[(**1**)+(**3**)]	R(**1**)	R(**3**)	Log P	[R(**3**)–R(**1**)]/[R(**3**)+R(**1**)]
1.00E+04	3.93E-19	2.38E-18	2.77E-18	13.95	84.49	4	0.7166
1.00E+02	3.93E-19	2.38E-18	2.77E-18	13.95	84.49	2	0.7166
1.00E+00	3.93E-19	2.36E-18	2.75E-18	14.06	84.44	0	0.7145
1.00E-02	3.41E-19	1.67E-18	2.01E-18	16.84	82.45	-2	0.6609
1.00E-04	6.23E-20	1.47E-19	2.09E-19	29.68	70.04	-4	0.4047
1.00E-06	1.57E-21	2.49E-21	4.06E-21	38.59	61.21	-6	0.2266
1.00E-08	1.78E-23	2.58E-23	4.36E-23	40.75	59.06	-8	0.1835
1.00E-10	1.78E-25	2.59E-25	4.37E-25	40.66	59.16	-10	0.1854
1.00E-12	1.78E-27	2.59E-27	4.37E-27	40.66	59.16	-12	0.1854

Table S3*b*: (*T*= 336 K; *syn* isomer)

P (bar)	k_{eff}(**1**)	k_{eff}(**3**)	k_{eff}[(**1**)+(**3**)]	*R*(**1**)	*R*(**3**)	Log *P*	[*R*(**3**)–*R*(**1**)]/[*R*(**3**)+*R*(**1**)]
1.00E+04	1.05E-18	5.29E-18	6.34E-18	16.10	81.13	4	0.6688
1.00E+02	1.05E-18	5.29E-18	6.34E-18	16.10	81.13	2	0.6688
1.00E+00	1.05E-18	5.23E-18	6.28E-18	16.29	81.14	0	0.6656
1.00E-02	8.13E-19	3.01E-18	3.82E-18	21.05	77.94	-2	0.5747
1.00E-04	9.23E-20	1.67E-19	2.59E-19	35.44	64.13	-4	0.2881
1.00E-06	1.76E-21	2.35E-21	4.11E-21	42.68	56.98	-6	0.1436
1.00E-08	1.91E-23	2.41E-23	4.32E-23	44.07	55.60	-8	0.1157
1.00E-10	1.91E-25	2.41E-25	4.32E-25	44.07	55.60	-10	0.1157
1.00E-12	1.91E-27	2.41E-27	4.32E-27	44.07	55.60	-12	0.1157

Table S3*c*: (*T*= 400 K; *syn* isomer)

P (bar)	k_{eff}(**1**)	k_{eff}(**3**)	k_{eff}[(**1**)+(**3**)]	*R*(**1**)	*R*(**3**)	Log *P*	[*R*(**3**)–*R*(**1**)]/[*R*(**3**)+*R*(**1**)]
1.00E+04	3.69E-18	1.47E-17	1.84E-17	18.94	75.43	4	0.5987
1.00E+02	3.69E-18	1.47E-17	1.84E-17	18.94	75.44	2	0.5987
1.00E+00	3.65E-18	1.43E-17	1.80E-17	19.36	75.86	0	0.5933
1.00E-02	2.13E-18	5.29E-18	7.42E-18	28.28	70.23	-2	0.4259
1.00E-04	1.15E-19	1.54E-19	2.69E-19	42.42	56.81	-4	0.1450
1.00E-06	1.60E-21	1.79E-21	3.39E-21	46.88	52.44	-6	0.0560
1.00E-08	1.65E-23	1.81E-23	3.46E-23	47.37	51.96	-8	0.0462
1.00E-10	1.65E-25	1.81E-25	3.46E-25	47.37	51.96	-10	0.0462
1.00E-12	1.65E-27	1.81E-27	3.46E-27	47.37	51.96	-12	0.0462

Table S3*d*: (*T*= 298 K; *anti* isomer)

P (bar)	k_{eff}(**2**)	k_{eff}(**4**)	k_{eff}[(**2**)+(**4**)]	*R*(**2**)	*R*(**4**)	Log *P*	[*R*(**4**)–*R*(**2**)]/[*R*(**4**)+*R*(**2**)]
1.00E+04	4.92E-21	3.90E-20	4.39E-20	0.17	1.38	4	0.7760
1.00E+02	4.92E-21	3.90E-20	4.39E-20	0.17	1.38	2	0.7760
1.00E+00	4.85E-21	3.71E-20	4.20E-20	0.17	1.33	0	0.7688
1.00E-02	2.72E-21	1.17E-20	1.44E-20	0.13	0.58	-2	0.6227
1.00E-04	1.85E-22	3.92E-22	5.77E-22	0.09	0.19	-4	0.3588
1.00E-06	3.11E-24	4.95E-24	8.06E-24	0.08	0.12	-6	0.2283
1.00E-08	3.26E-26	4.99E-26	8.25E-26	0.07	0.11	-8	0.2097
1.00E-10	3.26E-28	4.99E-28	8.25E-28	0.07	0.11	-10	0.2097
1.00E-12	3.26E-30	4.99E-30	8.25E-30	0.07	0.11	-12	0.2097

Table S3*e*: (*T*= 336 K; *anti* isomer)

P (bar)	k_{eff}(**2**)	k_{eff}(**4**)	k_{eff}[(**2**)+(**4**)]	*R*(**2**)	*R*(**4**)	Log *P*	[*R*(**4**)–*R*(**2**)]/[*R*(**4**)+*R*(**2**)]
1.00E+04	2.45E-20	1.56E-19	1.81E-19	0.38	2.39	4	0.7285
1.00E+02	2.45E-20	1.56E-19	1.81E-19	0.38	2.39	2	0.7285
1.00E+00	2.37E-20	1.42E-19	1.66E-19	0.37	2.20	0	0.7139
1.00E-02	9.79E-21	2.94E-20	3.92E-20	0.25	0.76	-2	0.5004
1.00E-04	4.26E-22	6.97E-22	1.12E-21	0.16	0.27	-4	0.2413
1.00E-06	6.04E-24	8.05E-24	1.41E-23	0.15	0.20	-6	0.1427
1.00E-08	6.21E-26	8.09E-26	1.43E-25	0.14	0.19	-8	0.1315
1.00E-10	6.21E-28	8.09E-28	1.43E-27	0.14	0.19	-10	0.1315
1.00E-12	6.21E-30	8.09E-30	1.43E-29	0.14	0.19	-12	0.1315

Table S3*f*: (*T*= 400 K; *anti* isomer)

P (bar)	k_{eff}(**2**)	k_{eff}(**4**)	k_{eff}[(**2**)+(**4**)]	*R*(**2**)	*R*(**4**)	Log *P*	[*R*(**4**)–*R*(**2**)]/[*R*(**4**)+*R*(**2**)]
1.00E+04	1.87E-19	9.10E-19	1.10E-18	0.96	4.67	4	0.6591
1.00E+02	1.87E-19	9.08E-19	1.10E-18	0.96	4.66	2	0.6584
1.00E+00	1.72E-19	7.29E-19	9.01E-19	0.91	3.87	0	0.6182
1.00E-02	3.87E-20	7.40E-20	1.13E-19	0.51	0.98	-2	0.3132
1.00E-04	9.32E-22	1.16E-21	2.09E-21	0.34	0.43	-4	0.1090
1.00E-06	1.09E-23	1.22E-23	2.31E-23	0.32	0.36	-6	0.0563
1.00E-08	1.11E-25	1.23E-25	2.34E-25	0.32	0.35	-8	0.0513
1.00E-10	1.11E-27	1.23E-27	2.34E-27	0.32	0.35	-10	0.0513
1.00E-12	1.11E-29	1.23E-29	2.34E-29	0.32	0.35	-12	0.0513