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Electronic Supplementary Information for:

INTRAMOLECULAR EFFECTS ON THE KINETICS OF UNIMOLECULAR REACTIONS OF β-HOROO• AND HOQ•OOH RADICALS

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S1) Optimized geometries (Cartesian coordinates), electronic energies and ZPE (in hartree) at the m06/6-311+g(3df,2p) level of theory of the conformers of species from table 1

1a) 2-C_4H_9OH

Structure 1			
C	-2.044663	-0.029036	0.109229
H	-2.170851	-0.003190	1.195045
H	-2.092534	0.998100	-0.252836
H	-2.891392	-0.574901	-0.309170
C	-0.727375	-0.674539	-0.265990
H	-0.704251	-1.716754	0.069835
H	-0.605375	-0.692363	-1.355459
C	0.472036	0.034432	0.322282
H	0.343134	0.080478	1.417638
C	1.764125	-0.682128	0.002712
H	1.892978	-0.756895	-1.079887
H	2.626289	-0.148786	0.411884
H	1.767594	-1.689896	0.423481
O	0.475622	1.349213	-0.206316
H	1.244701	1.818121	0.120594
E_{0K} = -233.5876321		ZPE = 0.135765	

Structure 3			
C	-2.033342	-0.069012	0.085734
H	-2.154554	0.053862	1.166052
H	-2.138015	0.915510	-0.377972
H	-2.869094	-0.671789	-0.271234
C	-0.700117	-0.708350	-0.244698
H	-0.673202	-1.731983	0.144770
H	-0.568553	-0.779298	-1.330632
C	0.487547	0.044436	0.327740
H	0.370873	0.090364	1.424579
C	1.791865	-0.632954	-0.002933
H	1.920242	-0.681618	-1.087033
H	2.632902	-0.078207	0.413281
H	1.813148	-1.649208	0.394106
O	0.575375	1.359757	-0.190141
H	-0.212469	1.849592	0.050152
E_{0K} = -233.5875315		ZPE = 0.135853	

Structure 2			
C	2.045366	-0.048169	-0.106317
H	2.188821	-0.095703	-1.188902
H	2.086155	1.002926	0.181640
H	2.886396	-0.561197	0.362034
C	0.721232	-0.667695	0.286629
H	0.692727	-1.723660	-0.004634
H	0.598459	-0.652125	1.378819
C	-0.473100	0.036273	-0.332065
H	-0.333824	0.070025	-1.420227
C	-1.770997	-0.670275	-0.013751
H	-1.920125	-0.719857	1.070456
H	-2.618013	-0.139905	-0.449836
H	-1.768758	-1.694178	-0.393109
O	-0.528539	1.397121	0.057353
H	-0.718534	1.435902	0.997969
E_{0K} = -233.5871333		ZPE = 0.135597	

Structure 4			
C	2.026933	0.070537	0.111170
H	2.066005	1.079410	-0.304486
H	2.113693	0.158227	1.197853
H	2.910139	-0.460210	-0.245658
C	0.756128	-0.654880	-0.280399
H	0.634029	-0.663222	-1.369636
H	0.805041	-1.702260	0.030899
C	-0.494379	-0.056219	0.325637
H	-0.380396	-0.058663	1.423583
C	-0.755701	1.360162	-0.136129
H	-0.813151	1.394945	-1.227414
H	-1.700210	1.735397	0.267033
H	0.030776	2.041239	0.193733
O	-1.559661	-0.912662	-0.044315
H	-2.386527	-0.541167	0.266939
E_{0K} = -233.5871378		ZPE = 0.135994	

Structure 5			
C	-2.027631	0.059094	-0.090992
H	-2.071610	1.056076	0.351234
H	-2.118662	0.174929	-1.174650
H	-2.905104	-0.488488	0.254661
C	-0.745985	-0.665046	0.270321
H	-0.621375	-0.688564	1.362056
H	-0.793542	-1.707642	-0.057077
C	0.500320	-0.049046	-0.339464
H	0.391887	-0.054346	-1.431596
C	0.745757	1.369595	0.125518
H	0.809069	1.405405	1.219116
H	1.684323	1.744960	-0.283272
H	-0.054993	2.043845	-0.183058
O	1.631776	-0.861903	-0.088482
H	1.791025	-0.878537	0.858137
E_{0K} = -233.5866582		ZPE = 0.135729	

Structure 7			
C	1.742395	0.137083	-0.507903
H	1.484852	-0.569061	-1.298715
H	1.618187	1.146557	-0.905608
H	2.800839	0.010047	-0.276959
C	0.888056	-0.096955	0.722792
H	1.145511	-1.059458	1.174769
H	1.093019	0.667575	1.479912
C	-0.605209	-0.105423	0.458037
H	-1.110914	-0.233060	1.428762
C	-1.109980	1.168788	-0.183279
H	-0.680882	1.296545	-1.179020
H	-2.198255	1.149571	-0.284941
H	-0.849240	2.040714	0.421454
O	-0.874411	-1.230553	-0.360818
H	-1.799406	-1.225971	-0.610988
E_{0K} = -233.5866519		ZPE = 0.136167	

Structure 6			
C	2.025195	0.057221	0.105448
H	2.073684	1.065773	-0.308789
H	2.107112	0.143183	1.192577
H	2.904222	-0.482316	-0.248655
C	0.744512	-0.649096	-0.291370
H	0.619803	-0.646280	-1.380385
H	0.799383	-1.702841	0.010601
C	-0.502256	-0.042869	0.327247
H	-0.383950	-0.053128	1.424981
C	-0.752552	1.374883	-0.119936
H	-0.808820	1.419108	-1.210903
H	-1.698695	1.735860	0.283917
H	0.040167	2.044107	0.216182
O	-1.653963	-0.782101	-0.034830
H	-1.510591	-1.707494	0.170780
E_{0K} = -233.5872464		ZPE = 0.135853	

Structure 8			
C	1.746730	0.140054	-0.491941
H	1.583455	-0.665079	-1.213486
H	1.561955	1.088792	-1.000387
H	2.805147	0.116076	-0.230203
C	0.878550	-0.028296	0.739829
H	1.162417	-0.943444	1.267805
H	1.054126	0.800976	1.434275
C	-0.615726	-0.105831	0.456682
H	-1.127217	-0.233916	1.417233
C	-1.161895	1.132498	-0.220701
H	-0.738046	1.251607	-1.222466
H	-2.245185	1.063800	-0.322953
H	-0.922215	2.033416	0.348962
O	-0.947787	-1.271671	-0.275518
H	-0.638091	-1.169408	-1.177845
E_{0K} = -233.5860657		ZPE = 0.136032	

Structure 9			
C	1.740544	0.168853	-0.492692
H	1.470937	-0.482040	-1.326575
H	1.629987	1.201024	-0.830258
H	2.796922	0.011658	-0.271259
C	0.878054	-0.117695	0.720588
H	1.142195	-1.095931	1.142010
H	1.080410	0.611628	1.513272
C	-0.618712	-0.114717	0.444253
H	-1.134365	-0.271520	1.405348
C	-1.113337	1.175639	-0.159387
H	-0.689817	1.317575	-1.155383
H	-2.198857	1.158702	-0.257040
H	-0.831906	2.027624	0.462916
O	-0.984560	-1.145177	-0.457722
H	-0.708317	-1.989782	-0.097825
E_{0K} = -233.5867815		ZPE = 0.136197	

1b) $C_2H_4(OH)OO•$

Structure 1			
C	1.109789	0.447880	-0.317237
H	0.957889	0.442080	-1.406883
H	1.915215	1.157449	-0.109720
O	1.518919	-0.796772	0.162092
H	0.758789	-1.388215	0.138482
C	-0.145956	0.962337	0.339223
H	-0.132264	0.787075	1.417598
H	-0.308228	2.020358	0.130758
O	-1.326144	0.321872	-0.199576
O	-1.314575	-0.960106	-0.000285
E_{0K} = -304.6871528		ZPE = 0.077052	

Structure 2			
C	1.238443	0.461556	-0.160803
H	1.277591	0.661902	-1.239396
H	1.986744	1.105558	0.323341
O	1.446691	-0.892560	0.128025
H	2.174878	-1.232954	-0.391666
C	-0.113932	0.848531	0.357166
H	-0.268680	0.501542	1.379449
H	-0.261417	1.928521	0.291049
O	-1.137197	0.248254	-0.463693
O	-1.766516	-0.708831	0.143048
E_{0K} = -304.682289		ZPE = 0.076337	

Structure 3			
C	1.003292	0.173495	0.589968
H	1.636934	0.914716	1.096309
H	0.588496	-0.478631	1.361640
O	1.733938	-0.643767	-0.280447
H	2.183864	-0.105176	-0.933442
C	-0.126676	0.903808	-0.084594
H	-0.627235	1.583054	0.609450
H	0.211836	1.459507	-0.962675
O	-1.116168	-0.008893	-0.602804
O	-1.774470	-0.577001	0.357809
E_{0K} = -304.6832307		ZPE = 0.076728	

Structure 4			
C	1.023172	0.277804	0.544915
H	1.707475	1.061784	0.877296
H	0.629939	-0.217321	1.441598
O	1.759376	-0.599123	-0.261019
H	1.210751	-1.352256	-0.490170
C	-0.117593	0.919511	-0.195976
H	-0.632062	1.666076	0.412054
H	0.213669	1.351655	-1.141031
O	-1.088978	-0.082456	-0.583365
O	-1.740804	-0.530148	0.445212
E_{0K} = -304.6864821		ZPE = 0.076795	

Structure 5			
C	0.996647	0.184008	0.581044
H	1.609527	0.926452	1.111059
H	0.580057	-0.500844	1.329433
O	1.732175	-0.490160	-0.405227
H	2.289177	-1.155135	-0.000851
C	-0.133727	0.904640	-0.087490
H	-0.636684	1.583592	0.603280
H	0.212342	1.444817	-0.969597
O	-1.121903	-0.019201	-0.595440
O	-1.764265	-0.594485	0.371336
E_{0K} = -304.6846053		ZPE = 0.076451	

Structure 6			
C	-0.908554	-0.328818	0.369346
H	-0.567485	-1.344769	0.139934
H	-0.932878	-0.229147	1.456594
O	-2.204177	-0.075732	-0.101798
H	-2.288669	-0.398755	-1.000251
C	0.073243	0.666764	-0.210502
H	0.116344	0.603219	-1.300728
H	-0.170313	1.686205	0.090637
O	1.392172	0.417072	0.304985
O	1.918862	-0.634394	-0.245594
E_{0K} = -304.6832233		ZPE = 0.076715	

Structure 7			
C	-0.900039	-0.384028	0.301976
H	-0.572167	-1.368572	-0.037154
H	-0.885836	-0.393824	1.398638
O	-2.184251	-0.165910	-0.215666
H	-2.601448	0.561825	0.247461
C	0.068774	0.658295	-0.213502
H	0.130356	0.637449	-1.302624
H	-0.199101	1.662679	0.122921
O	1.380414	0.424509	0.328895
O	1.943310	-0.601744	-0.233240
E_{0K} = -304.682705		ZPE = 0.076817	

Structure 8			
C	-0.899911	-0.376268	0.297185
H	-0.575998	-1.353772	-0.080485
H	-0.886504	-0.415794	1.394463
O	-2.154779	0.001628	-0.203882
H	-2.810744	-0.654957	0.030876
C	0.073581	0.673072	-0.175058
H	0.129072	0.704902	-1.264186
H	-0.187872	1.658196	0.212950
O	1.383795	0.392478	0.346713
O	1.932238	-0.609031	-0.271129
E_{0K} = -304.6833291		ZPE = 0.076660	

Structure 9			
C	-1.264708	0.491362	0.245891
H	-1.265169	0.532648	1.343365
H	-1.908079	1.300130	-0.106636
O	-1.809399	-0.707912	-0.229135
H	-1.300035	-1.443571	0.117722
C	0.127940	0.729478	-0.260812
H	0.198939	0.600236	-1.342389
H	0.514585	1.710649	0.025501
O	0.964259	-0.275752	0.356666
O	2.167686	-0.269477	-0.121036
E_{0K} = -304.6854554		ZPE = 0.076679	

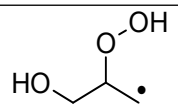
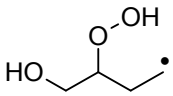
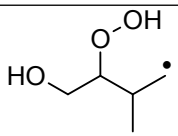
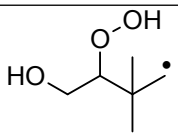
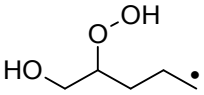
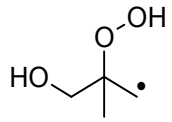
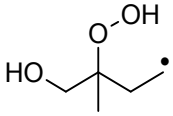
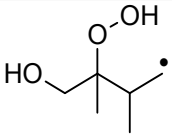
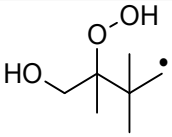
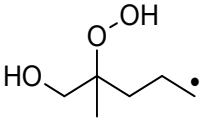
Structure 10			
C	1.247518	0.500806	-0.249973
H	1.212947	0.555130	-1.340593
H	1.852447	1.350416	0.094634
O	1.833182	-0.730689	0.066702
H	1.939281	-0.805548	1.016693
C	-0.140585	0.660349	0.299093
H	-0.195095	0.441858	1.369771
H	-0.532000	1.665923	0.122556
O	-1.001855	-0.274605	-0.380587
O	-2.196224	-0.266545	0.119162
E_{0K} = -304.6823577		ZPE = 0.076388	

Structure 11			
C	-1.117000	0.506588	0.016254
H	-1.086248	1.108653	0.932684
H	-1.106284	1.203772	-0.823951
O	-2.295022	-0.247031	-0.087623
H	-2.448069	-0.721056	0.731270
C	0.094381	-0.391917	-0.051254
H	0.133502	-1.095940	0.785206
H	0.128949	-0.951767	-0.988301
O	1.255970	0.453843	0.022937
O	2.353285	-0.235773	0.011321
E_{0K} = -304.6812532		ZPE = 0.076391	

Structure 12			
C	1.111029	0.495035	0.000189
H	1.085051	1.143347	-0.885313
H	1.085745	1.143137	0.885860
O	2.226023	-0.356393	-0.000276
H	3.030858	0.161873	-0.000768
C	-0.097614	-0.401093	0.000436
H	-0.132573	-1.033528	-0.889007
H	-0.132966	-1.032868	0.890333
O	-1.249922	0.458773	-0.000077
O	-2.353177	-0.220582	-0.000254
E_{0K} = -304.6818343		ZPE = 0.076344	

S2) Structures of the HOQ•OOH radicals corresponding to internal H-transfers of radicals from table 3

2a) Group 1

β-HOROO•	γ-HOQ•OOH			δ-HOQ•OOH
				
R_2	**R_{19}**	**R_{21}**	**R_{35}**	**R_{23}**
				
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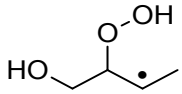
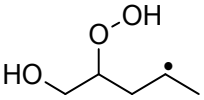
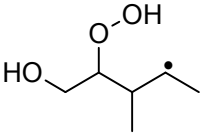
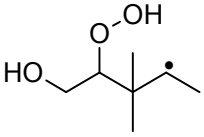
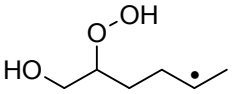
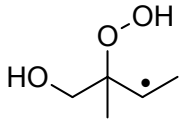
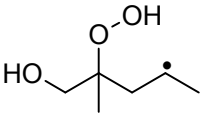
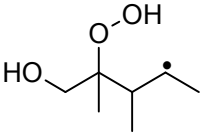
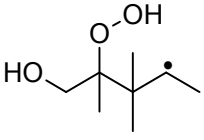
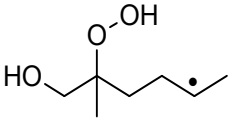
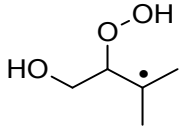
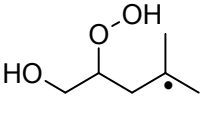
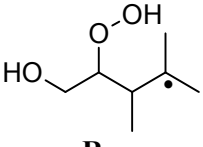
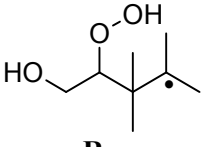
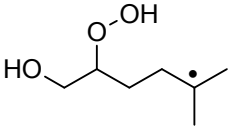
				
R_{19}	**R_{23}**	**R_{42}**	**R_{47}**	**R_{27}**
				
R_{20}	**R_{24}**	**R_{43}**	**R_{48}**	**R_{28}**
				
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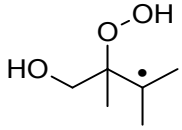
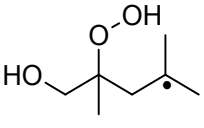
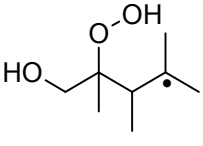
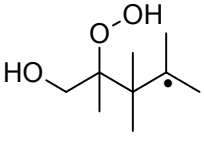
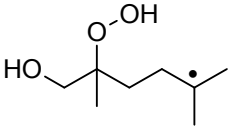
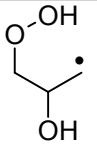
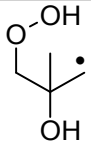
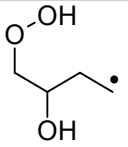
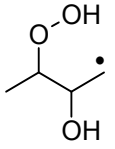
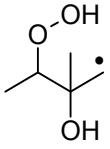
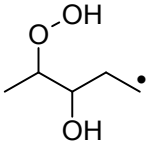
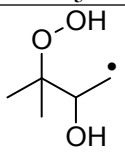
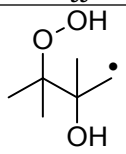
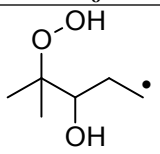
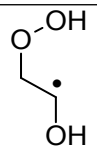
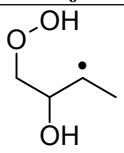
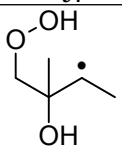
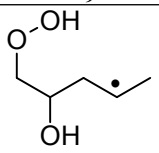
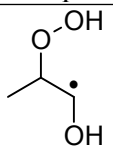
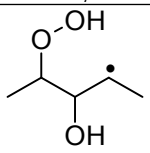
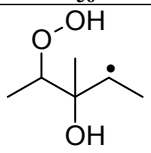
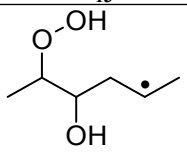
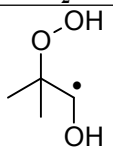
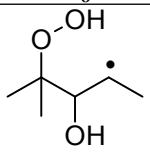
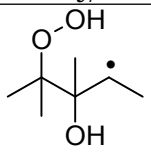
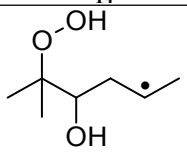
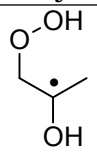
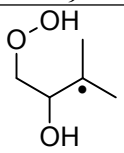
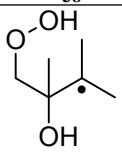
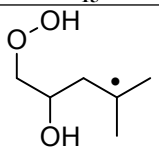
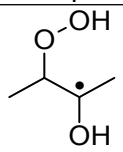
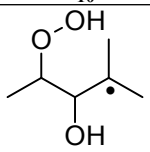
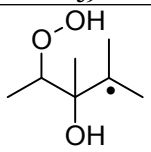
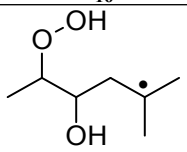
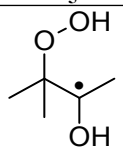
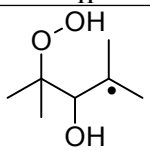
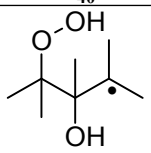
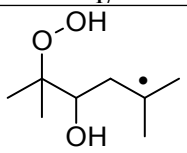
				
R_{22}	**R_{26}**	**R_{45}**	**R_{50}**	**R_{30}**

2b) Group 2

β-HOQ•OOH	γ-HOQ•OOH		δ-HOQ•OOH
	 **R_4**	 **R_{32}**	 **R_7**
	 **R_5**	 **R_{33}**	 **R_8**
	 **R_6**	 **R_{34}**	 **R_9**
 **R_1**	 **R_7**	 **R_{36}**	 **R_{13}**
 **R_2**	 **R_8**	 **R_{37}**	 **R_{14}**
 **R_3**	 **R_9**	 **R_{38}**	 **R_{15}**
 **R_4**	 **R_{10}**	 **R_{39}**	 **R_{16}**
 **R_5**	 **R_{11}**	 **R_{40}**	 **R_{17}**
 **R_6**	 **R_{12}**	 **R_{41}**	 **R_{18}**

S3) Modified Arrhenius Fits of the unimolecular reactions of β-HOROO• and HOQ•OOH radicals. Units: A (s^{-1}) and E (cal mol^{-1})

3a) For 1,5 H-shift of β-HOROO• radicals from **Table 4**

R	Reaction HOROO• (group 1) → γ-HOQ•OOH	C_{-OO}	H_{arr}	$k = AT^n exp(-E/RT)$ A	n	E
19	HOCC(OO•)CC → HOCC(OOH)CC•	t	p	6.23×10^{3}	2.35	18430
20	HOC(C)C(OO•)CC → HOC(C)C(OOH)CC•	q	p	1.04×10^{6}	1.78	19403
23	HOCC(OO•)CCC → HOCC(OOH)CC•C	t	s	7.15×10^{5}	1.67	16221
24	HOC(C)C(OO•)CCC → HOC(C)C(OOH)CC•C	q	s	2.04×10^{7}	1.21	16239
25	HOCC(OO•)CCC$_2$ → HOCC(OOH)CC•C$_2$	t	t	4.77×10^{6}	1.35	13588
26	HOC(C)C(OO•)CCC$_2$ → HOC(C)C(OOH)CC•C$_2$	q	t	1.39×10^{6}	1.51	12811
R	**Reaction** HOROO• (group 2) → γ-HOQ•OOH	C_{-OO}	H_{arr}	$k = AT^n exp(-E/RT)$ A	n	E
4	C(OO•)C(OH)C → C(OOH)C(OH)C•	s	p	1.53×10^{5}	2.05	20330
5	CC(OO•)C(OH)C → CC(OOH)C(OH)C•	t	p	4.12×10^{4}	2.20	19784
6	C$_2$C(OO•)C(OH)C → C$_2$C(OOH)C(OH)C•	q	p	2.22×10^{6}	1.81	21013
7	C(OO•)C(OH)CC → C(OOH)C(OH)C•C	s	s	5.76×10^{6}	1.54	17944
8	CC(OO•)C(OH)CC → CC(OOH)C(OH)C•C	t	s	2.34×10^{7}	1.41	17829
9	C$_2$C(OO•)C(OH)CC → C$_2$C(OOH)C(OH)C•C	q	s	2.27×10^{9}	0.83	18664
10	C(OO•)C(OH)CC$_2$ → C(OOH)C(OH)C•C$_2$	s	t	3.86×10^{7}	1.21	15665
11	CC(OO•)C(OH)CC$_2$ → CC(OOH)C(OH)C•C$_2$	t	t	4.42×10^{8}	0.97	15399
12	C$_2$C(OO•)C(OH)CC$_2$ → C$_2$C(OOH)C(OH)C•C$_2$	q	t	3.92×10^{11}	0.17	16655

3b) For 1,6 H-shift of β-HOROO• radicals from **Table 5**

R	Réaction HOROO• (groupe 1) → δ-HOQ•OOH	C_{-OO}	H_{arr}	$k = AT^n exp(-E/RT)$		
				A	n	E
23	HOCC(OO•)CCC→ HOCC(OOH)CCC•	t	p	2.29×10^{2}	2.53	17005
24	HOC(C)C(OO•)CCC→ HOC(C)C(OOH)CCC•	q	p	2.13×10^{6}	1.38	18485
27	HOCC(OO•)CCCC→ HOCC(OOH)CCC•C	t	s	8.68×10^{2}	2.31	13600
28	HOC(C)C(OO•)CCCC→ HOC(C)C(OOH)CCC•C	q	s	6.09×10^{6}	1.20	15177
29	$HOCC(OO•)CCCC_2$→ $HOCC(OOH)CCC•C_2$	t	t	2.72×10^{3}	2.16	11165
30	$HOC(C)C(OO•)CCCC_2$→ $HOC(C)C(OOH)CCC•C_2$	q	t	7.49×10^{7}	0.83	12793

R	Réaction HOROO• (groupe 2) → δ-HOQ•OOH	C_{-OO}	H_{arr}	$k = AT^n exp(-E/RT)$		
				A	n	E
7	C(OO•)C(OH)CC → C(OOH)C(OH)CC•	s	p	8.48×10^{5}	1.59	19515
8	CC(OO•)C(OH)CC → CC(OOH)C(OH)CC•	t	p	7.43×10^{6}	1.34	20054
9	$C_2C(OO•)C(OH)CC$ → $C_2C(OOH)C(OH)CC•$	q	p	1.82×10^{9}	0.68	20655
13	C(OO•)C(OH)CCC → C(OOH)C(OH)CC•C	s	s	8.36×10^{6}	1.26	16333
14	CC(OO•)C(OH)CCC → CC(OOH)C(OH)CC•C	t	s	2.64×10^{7}	1.16	16609
15	$C_2C(OO•)C(OH)CCC$ → $C_2C(OOH)C(OH)CC•C$	q	s	2.44×10^{9}	0.62	17748
16	$C(OO•)C(OH)CCC_2$ → $C(OOH)C(OH)CC•C_2$	s	t	4.56×10^{9}	0.40	14918
17	$CC(OO•)C(OH)CCC_2$ → $CC(OOH)C(OH)CC•C_2$	t	t	5.25×10^{10}	0.10	15442
18	$C_2C(OO•)C(OH)CCC_2$ → $C_2C(OOH)C(OH)CC•C_2$	q	t	4.13×10^{12}	-0.39	16335

3c) For 1,4 H-shift of β-HOROO• radicals from **Table 7**

R	Réaction HOROO• (groupe 1) → β-HOQ•OOH	C_{-OO}	H_{arr}	k = $AT^n exp(-E/RT)$		
				A	n	E
2	HOCC(OO•)C → HOCC(OOH)C•	t	p	1.35×10^{-3}	4.55	26985
3	HOC(C)C(OO•)C→ HOC(C)C(OOH)C•	q	p	9.48×10^{-1}	3.73	26469
19	HOCC(OO•)CC→ HOCC(OOH)C•C	t	s	2.77×10^{-1}	3.77	23992
20	HOC(C)C(OO•)CC→ HOC(C)C(OOH)C•C	q	s	1.43×10^{3}	2.76	24752
21	HOCC(OO•)CC_2→ HOCC(OOH)C•C_2	t	t	1.52×10^{3}	2.64	22082
22	HOC(C)C(OO•)CC_2 → HOC(C)C(OOH)C•C_2	q	t	6.12×10^{3}	2.47	21089

R	Réaction HOROO• (groupe 2) → β-HOQ•OOH	C_{-OO}	H_{arr}	k = $AT^n exp(-E/RT)$		
				A	n	E
1	C(OO•)COH → C(OOH)C•(OH)	s	s	9.28×10^{3}	2.46	21874
2	CC(OO•)COH → CC(OOH)C•(OH)	t	s	1.76×10^{3}	2.69	21498
3	C_2C(OO•)COH → C_2C(OOH)C•(OH)	q	s	1.19×10^{6}	1.94	22661
4	C(OO•)C(OH)C → C(OOH)C•(OH)C	s	t	1.92×10^{5}	2.03	20190
5	CC(OO•)C(OH)C → CC(OOH)C•(OH)C	t	t	2.85×10^{5}	2.00	19560
6	C_2C(OO•)C(OH)C → C_2C(OOH)C•(OH)C	q	t	3.01×10^{6}	1.75	20103

3d) For HO_2• elimination from β-HOROO• radicals from **Table 8**

R	Réaction HOROO• (groupe 1) → énol + HO_2•	C_{-OO}	H_{arr}	k = $AT^n exp(-E/RT)$		
				A	n	E
2	HOCC(OO•)C → HOCC=C+ HO_2•	t	p	3.86×10^7	1.48	29631
3	HOC(C)C(OO•)C → HOC(C)C=C + HO_2•	q	p	3.03×10^9	1.22	29419
19	HOCC(OO•)CC → HOCC=CC+ HO_2•	t	s	3.15×10^7	1.58	28744
20	HOC(C)C(OO•)CC → HOC(C)C=CC + HO_2•	q	s	3.89×10^9	1.07	29027
21	HOCC(OO•)CC_2 → HOCC=CC_2+ HO_2•	t	t	6.96×10^7	1.49	28328
22	HOC(C)C(OO•)CC_2 → HOC(C)C=CC_2 + HO_2•	q	t	2.38×10^{11}	0.59	29894
R	**Réaction** HOROO• (groupe 2) → énol + HO_2•	C_{-OO}	H_{arr}	k = $AT^n exp(-E/RT)$		
				A	n	E
1	C(OO•)COH → C=COH + HO_2•	s	s	1.49×10^{13}	0.03	33209
2	CC(OO•)COH → CC=COH + HO_2•	t	s	2.07×10^{13}	0.00	32999
3	C_2C(OO•)COH → C_2C=COH + HO_2•	q	s	2.26×10^{16}	-0.82	33642
4	C(OO•)C(OH)C → C=C(OH)C + HO_2•	s	t	3.65×10^{13}	-0.15	34790
5	CC(OO•)C(OH)C → CC=C(OH)C + HO_2•	t	t	6.12×10^{14}	-0.47	34516
6	C_2C(OO•)C(OH)C → C_2C=C(OH)C + HO_2•	q	t	1.01×10^{17}	-1.01	35174

3e) For cyclic ether formation from β-, γ-, and δ-HOQ•OOH radicals from **Table 9** - Group 1

R	Reaction β-HOQ•OOH (group 1) → hydroxy-oxirane + •OH	C_{-OOH}	C•	k = $AT^n exp(-E/RT)$		
				A	n	E
2	HOCC(OOH)C• → HOC-cycle[CCO] + •OH	t	p	2.26×10^{10}	0.56	10498
3	HOC(C)C(OOH)C• → HOC(C)-cycle[CCO] + •OH	q	p	4.31×10^{11}	0.10	9747
19	HOCC(OOH)C•C → HOC-cycle[CCO]-C + •OH	t	s	2.76×10^{9}	1.01	8031
20	HOC(C)C(OOH)C•C → HOC(C)cycle[CCO]-C + •OH	q	s	2.70×10^{11}	0.11	7546
21	HOCC(OOH)C•C_2 → HOC-cycle[CCO]-C_2 + •OH	t	t	7.46×10^{10}	0.18	7515
22	HOC(C)C(OOH)C•C_2 → HOC(C)-cycle[CCO]-C_2 + •OH	q	t	8.35×10^{9}	0.51	7153

R	Reaction γ-HOQ•OOH (group 1) → hydroxy-oxetane + •OH	C_{-OOH}	C•	k = $AT^n exp(-E/RT)$		
				A	n	E
19	HOCC(OOH)CC•→ HOC-cycle[CCCO] + •OH	t	p	1.67×10^{11}	-0.09	16142
20	HOC(C)C(OOH)CC• → HOC(C)-cycle[CCCO] + •OH	q	p	3.75×10^{10}	0.13	13486
23	HOCC(OOH)CC•C → HOC-cycle[CCCO] + •OH	t	s	2.44×10^{11}	-0.08	12763
24	HOC(C)C(OOH)CC•C → HOC(C)-cycle[CCCO] + •OH	q	s	1.13×10^{11}	0.01	12001
25	HOCC(OOH)CC•C_2 → HOC-cycle[CCCO]-C_2 + •OH	t	t	8.09×10^{10}	0.08	11242
26	HOC(C)C(OOH)CC•C_2 → HOC(C)-cycle[CCCO]-C_2 + •OH	q	t	9.77×10^{10}	0.17	10400

R	Reaction δ-HOQ•OOH (group 1) → hydroxy-oxolane + •OH	C_{-OOH}	C•	k = $AT^n exp(-E/RT)$		
				A	n	E
23	HOCC(OOH)CCC•→ HOC-cycle[CCCCO] + •OH	t	p	5.02×10^{12}	-0.77	10632
24	HOC(C)C(OOH)CCC• → HOC(C)-cycle[CCCCO] + •OH	q	p	4.00×10^{12}	-0.64	9932
27	HOCC(OOH)CCC•C → HOC-cycle[CCCCO] + •OH	t	s	7.59×10^{13}	-1.08	9093
28	HOC(C)C(OOH)CCC•C → HOC(C)-cycle[CCCCO] + •OH	q	s	5.01×10^{14}	-1.30	8933
29	HOCC(OOH)CCC•C_2 → HOC-cycle[CCCCO]-C_2 + •OH	t	t	1.55×10^{15}	-1.42	7888
30	HOC(C)C(OOH)CCC•C_2 → HOC(C)-cycle[CCCCO]-C_2 + •OH	q	t	1.21×10^{17}	-1.92	8510

3f) For cyclic ether formation from β-, γ-, and δ-HOQ•OOH radicals from **Table 10** - Group 2

R	Reaction β-HOQ•OOH (group 2) → hydroxy-oxirane + •OH	C_{-OOH}	C•	k = $AT^n exp(-E/RT)$ A	n	E
1	C(OOH)C•(OH) → cycle[CC(OH)O] + •OH	s	s	3.11×10^{12}	0.06	11161
2	CC(OOH)C•(OH) → C-cycle[CC(OH)O] + •OH	t	s	3.90×10^{12}	0.02	9532
3	C_2C(OOH)C•(OH) → C_2-cycle[CC(OH)O] + •OH	q	s	9.88×10^{11}	0.15	7890
4	C(OOH)C•(OH)C → cycle[CC(OH)O]-C + •OH	s	t	8.62×10^{10}	0.56	9184
5	CC(OOH)C•(OH)C → C-cycle[CC(OH)O]-C + •OH	t	t	7.44×10^{10}	0.58	7568
6	C_2C(OOH)C•(OH)C → C_2-cycle[CC(OH)O]-C + •OH	q	t	5.56×10^{13}	-0.32	7804
R	**Reaction** γ-HOQ•OOH (group 2) → hydroxy-oxétane + •OH	C_{-OOH}	C•	k = $AT^n exp(-E/RT)$ A	n	E
4	C(OOH)C(OH)C• → cycle[CC(OH)CO] + •OH	s	p	2.31×10^{15}	-1.08	21617
5	CC(OOH)C(OH)C• → C-cycle[CC(OH)CO] + •OH	t	p	1.00×10^{16}	-1.33	19882
6	C_2C(OOH)C(OH)C• → C_2-cycle[CC(OH)CO] + •OH	q	p	5.03×10^{15}	-1.21	19263
7	C(OOH)C(OH)C•C → cycle[CC(OH)CO]C + •OH	s	s	6.83×10^{13}	-0.59	18410
8	CC(OOH)C(OH)C•C → C-cycle[CC(OH)CO]C + •OH	t	s	2.18×10^{14}	-0.76	17066
9	C_2C(OOH)C(OH)C•C → C_2-cycle[CC(OH)CO]C + •OH	q	s	3.69×10^{14}	-0.78	16261
10	C(OOH)C(OH)C•C_2 → cycle[CC(OH)CO]C_2 + •OH	s	t	1.55×10^{15}	-0.88	16666
11	CC(OOH)C(OH)C•C_2 → C-cycle[CC(OH)CO]C_2 + •OH	t	t	1.95×10^{15}	-0.88	15839
12	C_2C(OOH)C(OH)C•C_2 → C_2-cycle[CC(OH)CO]C_2 + •OH	q	t	3.09×10^{17}	-1.56	16115
R	**Reaction** δ-HOQ•OOH (group 2) → hydroxy-oxolane + •OH	C_{-OOH}	C•	k = $AT^n exp(-E/RT)$ A	n	E
7	C(OOH)C(OH)CC• → cycle[CC(OH)CCO] + •OH	s	p	1.93×10^{12}	-0.42	12689
8	CC(OOH)C(OH)CC• → C-cycle[CC(OH)CCO] + •OH	t	p	7.31×10^{11}	-0.31	12455
9	C_2C(OOH)C(OH)CC• → C_2-cycle[CC(OH)CCO] + •OH	q	p	1.02×10^{15}	-1.25	14452
13	C(OOH)C(OH)CC•C → cycle[CC(OH)CCO]C + •OH	s	s	1.90×10^{10}	0.05	10767
14	CC(OOH)C(OH)CC•C → C-cycle[CC(OH)CCO]C + •OH	t	s	3.89×10^{11}	-0.29	10716
15	C_2C(OOH)C(OH)CC•C → C_2-cycle[CC(OH)CCO]C + •OH	q	s	1.62×10^{13}	-0.76	12015
16	C(OOH)C(OH)CC•C_2 → cycle[CC(OH)CCO]C_2 + •OH	s	t	3.17×10^{10}	0.03	9292
17	CC(OOH)C(OH)CC•C_2 → C-cycle[CC(OH)CCO]C_2 + •OH	t	t	2.09×10^{11}	-0.18	9249
18	C_2C(OOH)C(OH)CC•C_2 → C_2-cycle[CC(OH)CCO]C_2 + •OH	q	t	1.25×10^{12}	-0.52	8175

3g) For β-scission of β-HOQ•OOH radicals from **Table 11**

R	Réaction β-HOQ•OOH (groupe 1) → énol + HO_2•	C_{-OOH}	C•	k = $AT^n exp(-E/RT)$		
				A	n	E
2	HOCC(OOH)C• → HOCC=C+ HO_2•	t	p	8.17×10^{9}	0.80	14231
3	HOC(C)C(OOH)C• → HOC(C)C=C + HO_2•	q	p	5.06×10^{10}	0.54	13832
19	HOCC(OOH)C•C → HOCC=CC+ HO_2•	t	s	1.97×10^{10}	0.74	14280
20	HOC(C)C(OOH)C•C → HOC(C)C=CC + HO_2•	q	s	1.00×10^{11}	0.48	13393
21	HOCC(OOH)C•C_2 → HOCC=CC_2+ HO_2•	t	t	2.26×10^{11}	0.43	13893
22	HOC(C)C(OOH)C•C_2 → HOC(C)C=CC_2 + HO_2•	q	t	2.66×10^{11}	0.45	13755

R	Réaction β-HOQ•OOH (groupe 2) → énol + HO_2•	C_{-OOH}	C•	k = $AT^n exp(-E/RT)$		
				A	n	E
1	C(OOH)C•(OH) → C=COH + HO_2•	s	s	3.25×10^{12}	0.33	15980
2	CC(OOH)C•(OH) → CC=COH + HO_2•	t	s	5.22×10^{14}	-0.24	16658
3	C_2C(OOH)C•(OH) → C_2C=COH + HO_2•	q	s	6.39×10^{14}	-0.35	16490
4	C(OOH)C•(OH)C → C=C(OH)C + HO_2•	s	t	5.46×10^{10}	0.92	14881
5	CC(OOH)C•(OH)C → CC=C(OH)C + HO_2•	t	t	1.22×10^{13}	0.24	15271
6	C_2C(OOH)C•(OH)C → C_2C=C(OH)C + HO_2•	q	t	2.23×10^{14}	-0.18	16442

3h) For substitution of H-atoms by methyl groups in the cyclic part of transition states involved in the 1,5 H-shift of β-HOROO• radicals from **Table 12** - Group 1

R	Reaction HOROO• (group 1) → γ-HOQ•OOH	C_{-OO}	H_{arr}	$k = AT^n exp(-E/RT)$ A	n	E
	Without substitution					
19	HOCC(OO•)CC → HOCC(OOH)CC•	t	p	6.23×10^3	2.35	18430
20	HOC(C)C(OO•)CC → HOC(C)C(OOH)CC•	q	p	1.04×10^6	1.78	19403
23	HOCC(OO•)CCC → HOCC(OOH)CC•C	t	s	7.15×10^5	1.67	16221
24	HOC(C)C(OO•)CCC → HOC(C)C(OOH)CC•C	q	s	2.04×10^7	1.21	16239
25	HOCC(OO•)CCC_2 → HOCC(OOH)CC•C_2	t	t	4.77×10^6	1.35	13588
26	HOC(C)C(OO•)CCC_2 → HOC(C)C(OOH)CC•C_2	q	t	1.39×10^6	1.51	12811
	First substitution					
21	HOCC(OO•)CC_2 → HOCC(OOH)C(C)C•	t	p	3.10×10^5	1.84	19281
22	HOC(C)C(OO•)CC_2 → HOC(C)C(OOH)C(C)C•	q	p	2.67×10^6	1.70	18609
42	HOCC(OO•)C(C)CC → HOCC(OOH)C(C)C•C	t	s	2.07×10^4	2.06	14389
43	HOC(C)C(OO•)C(C)CC → HOC(C)C(OOH)C(C)C•C	q	s	2.44×10^5	1.78	13844
44	HOCC(OO•)C(C)CC_2 → HOCC(OOH)C(C)C•C_2	t	t	1.56×10^6	1.50	13053
45	HOC(C)C(OO•)C(C)CC_2 → HOC(C)C(OOH)C(C)C•C_2	q	t	1.35×10^8	1.06	12964
	Second substitution					
35	HOCC(OO•)C(C_2)C → HOCC(OOH)C(C_2)C•	t	p	3.66×10^6	1.69	19284
46	HOC(C)C(OO•)C(C_2)C → HOC(C)C(OOH)C(C_2)C•	q	p	2.67×10^6	1.70	18609
47	HOCC(OO•)C(C_2)CC → HOCC(OOH)C(C_2)C•C	t	s	3.72×10^4	2.09	14706
48	HOC(C)C(OO•)C(C_2)CC → HOC(C)C(OOH)C(C_2)C•C	q	s	2.37×10^6	1.69	14313
49	HOCC(OO•)C(C_2)CC_2 → HOCC(OOH)C(C_2)C•C_2	t	t	3.21×10^6	1.48	12509
50	HOC(C)C(OO•)C(C_2)CC_2 → HOC(C)C(OOH)C(C_2)C•C_2	q	t	5.31×10^7	1.14	11632

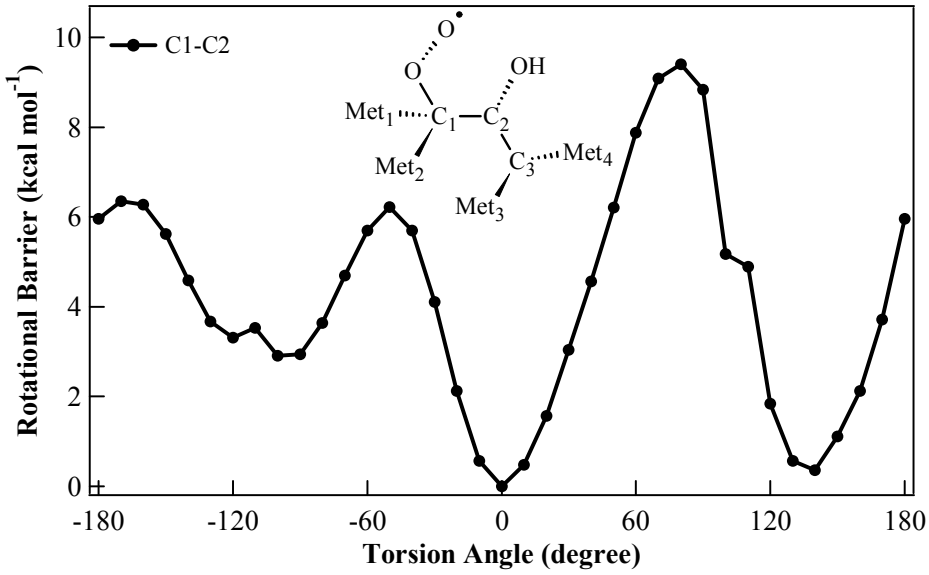
3i) For substitution of H-atoms by methyl groups in the cyclic part of transition states involved in the 1,5 H-shift of β-HOROO• radicals from **Table 13** - Group 2

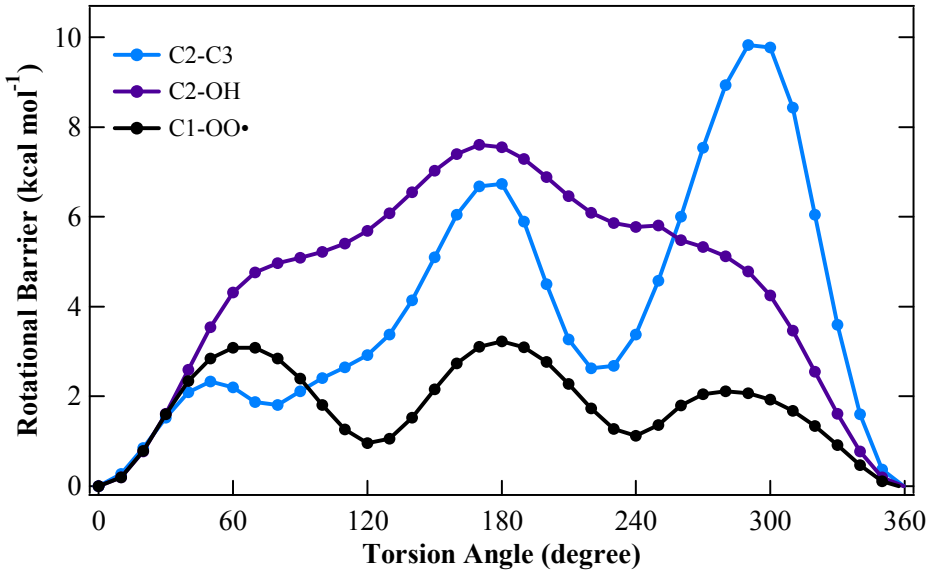
R	Reaction HOROO• (group 2) → γ-HOQ•OOH	C_{-OO}	H_{arr}	$k = AT^n\exp(-E/RT)$		
				A	n	E
	Without substitution					
4	C(OO•)C(OH)C → C(OOH)C(OH)C•	s	p	1.53×10^{5}	2.05	20330
5	CC(OO•)C(OH)C → CC(OOH)C(OH)C•	t	p	4.12×10^{4}	2.20	19784
6	C_2C(OO•)C(OH)C → C_2C(OOH)C(OH)C•	q	p	2.22×10^{6}	1.81	21013
7	C(OO•)C(OH)CC → C(OOH)C(OH)C•C	s	s	5.76×10^{6}	1.54	17944
8	CC(OO•)C(OH)CC → CC(OOH)C(OH)C•C	t	s	2.34×10^{7}	1.41	17829
9	C_2C(OO•)C(OH)CC → C_2C(OOH)C(OH)C•C	q	s	2.27×10^{9}	0.83	18664
10	C(OO•)C(OH)CC_2 → C(OOH)C(OH)C•C_2	s	t	3.86×10^{7}	1.21	15665
11	CC(OO•)C(OH)CC_2 → CC(OOH)C(OH)C•C_2	t	t	4.42×10^{8}	0.97	15399
12	C_2C(OO•)C(OH)CC_2 → C_2C(OOH)C(OH)C•C_2	q	t	3.92×10^{11}	0.17	16655
	With substitution					
32	C(OO•)C(OH)(C)C → C(OOH)C(OH)(C)C•	s	p	1.01×10^{7}	1.46	20173
33	CC(OO•)C(OH)(C)C → CC(OOH)C(OH)(C)C•	t	p	2.11×10^{5}	1.96	19816
34	C_2C(OO•)C(OH)(C)C → C_2C(OOH)C(OH)(C)C•	q	p	7.22×10^{5}	1.90	19784
36	C(OO•)C(OH)(C)CC → C(OOH)C(OH)(C)C•C	s	s	1.66×10^{5}	1.87	15190
37	CC(OO•)C(OH)(C)CC → CC(OOH)C(OH)(C)C•C	t	s	8.48×10^{4}	2.11	14922
38	C_2C(OO•)C(OH)(C)CC → C_2C(OOH)C(OH)(C)C•C	q	s	1.07×10^{6}	1.73	15736
39	C(OO•)C(OH)(C)CC_2 → C(OOH)C(OH)(C)C•C_2	s	t	5.42×10^{8}	0.78	14328
40	CC(OO•)C(OH)(C)CC_2 → CC(OOH)C(OH)(C)C•C_2	t	t	5.97×10^{7}	1.17	13441
41	C_2C(OO•)C(OH)(C)CC_2 → C_2C(OOH)C(OH)(C)C•C_2	q	t	6.82×10^{5}	1.74	11660

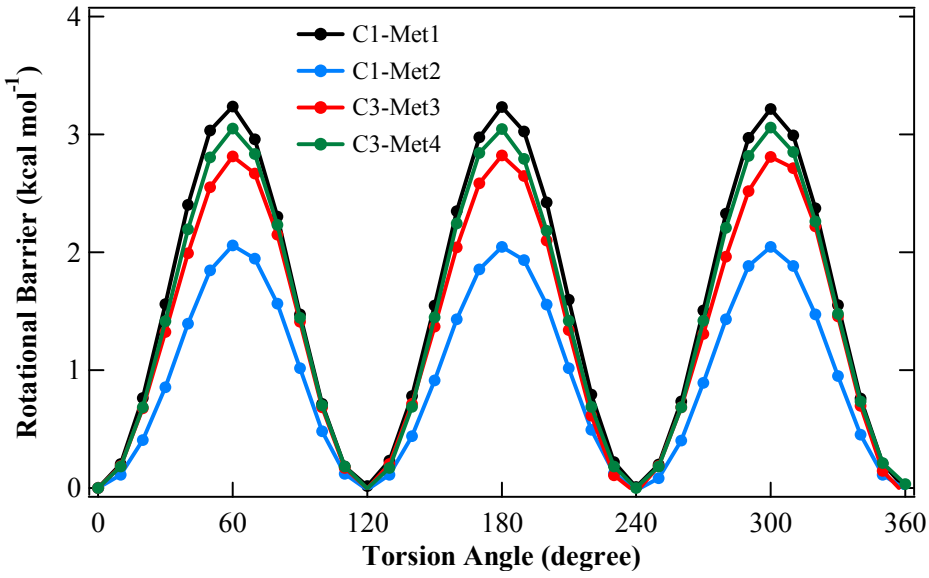
3j) For Waddington mechanism of β-HOROO• radicals from **Table 15**

R	Réaction HOROO• → R'=O + •OH	C_{-OO}	C_{-OH}	k	$k = AT^n\exp(-E/RT)$ A	n	E
	C(OO•)COH → C(OOH)CO•	s	s	k_1	8.84×10^{10}	0.12	21163
1	C(OOH)CO• → C(OO•)COH			k_{-1}	1.28×10^{12}	-0.23	-593
	C(OOH)CO• → 2 C=O+ •OH			k_2	4.42×10^{15}	-0.38	9847
	CC(OO•)COH → CC(OOH)CO•	t	s	k_1	2.61×10^{10}	0.29	20378
2	CC(OOH)CO• → CC(OO•)COH			k_{-1}	8.86×10^{15}	-1.36	1500
	CC(OOH)CO• → CC=O + C=O + •OH			k_2	1.99×10^{19}	-1.50	10820
	C_2C(OO•)COH → C_2C(OOH)CO•	q	s	k_1	5.75×10^{13}	-0.64	21610
3	C_2C(OOH)CO• → C_2C(OO•)COH			k_{-1}	1.09×10^{16}	-1.41	389
	C_2C(OOH)CO• → C_2C=O + C=O + •OH			k_2	6.35×10^{18}	-1.52	8047
	C(OO•)C(OH)CC → C(OOH)C(O•)CC	s	t	k_1	1.18×10^{10}	0.39	20322
7	C(OOH)C(O•)CC → C(OO•)C(OH)CC			k_{-1}	4.28×10^{17}	-1.94	2592
	C(OOH)C(O•)CC → C=O + CCC=O + •OH			k_2	8.69×10^{21}	-2.37	12629
	CC(OO•)C(OH)CC → CC(OOH)C(O•)CC	t	t	k_1	1.80×10^{11}	0.10	20330
8	CC(OOH)C(O•)CC → CC(OO•)C(OH)CC			k_{-1}	1.22×10^{17}	-1.71	1679
	CC(OOH)C(O•)CC → CC=O + CCC=O + •OH			k_2	4.72×10^{20}	-2.06	9465
	C_2C(OO•)C(OH)CC → C_2C(OOH)C(O•)CC	q	t	k_1	3.42×10^{12}	-0.22	20842
9	C_2C(OOH)C(O•)CC → C_2C(OO•)C(OH)CC			k_{-1}	4.39×10^{18}	-2.18	1440
	C_2C(OOH)C(O•)CC → C_2C=O + CCC=O + •OH			k_2	1.69×10^{23}	-2.87	7744
	C(OO•)C(OH)C_2 → C(OOH)C(O•)C_2	s	q	k_1	2.14×10^{13}	-0.62	22228
32	C(OOH)CO• → C(OO•)C(OH)C_2			k_{-1}	7.98×10^{18}	-2.15	3826
	C(OOH)C(O•)C_2 → C=O + C_2C=O + •OH			k_2	7.91×10^{22}	-2.61	12398
	CC(OO•)C(OH)C_2 → CC(OOH)C(O•)C_2	t	q	k_1	1.33×10^{11}	0.05	20310
33	CC(OOH)C(O•)C_2 → CC(OO•)C(OH)C_2			k_{-1}	5.80×10^{18}	-2.08	2899
	CC(OOH)C(O•)C_2 → CC=O + C_2C=O + •OH			k_2	3.43×10^{22}	-2.55	10499
34	C_2C(OO•)C(OH)C_2 → 2 C_2C=O + •OH	q	q	k_1	4.58×10^{14}	-0.82	22410

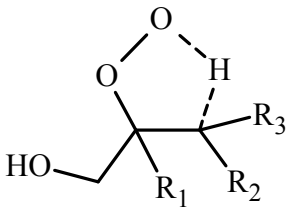
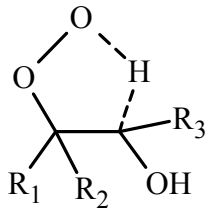
S4) Internal rotation potentials for the R12 radical [$(CH_3)_2$-C(OO•)-C(OH)-$CH(CH_3)_2$] calculated at B3LYP/6-311G(d,p) level

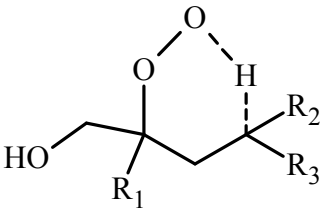
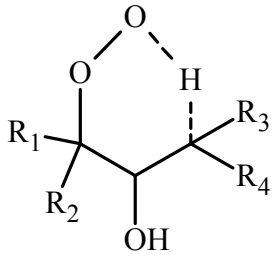


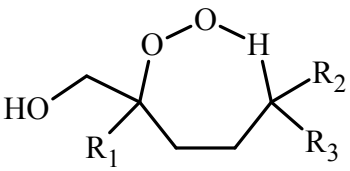
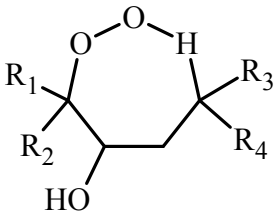


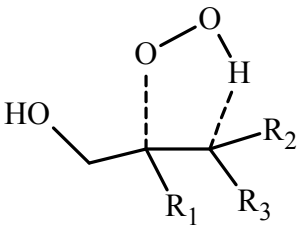
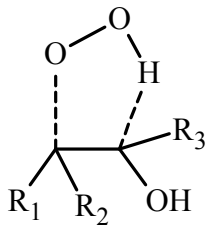


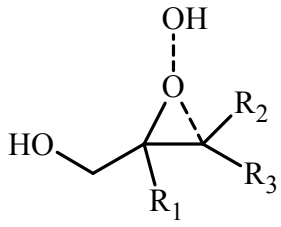
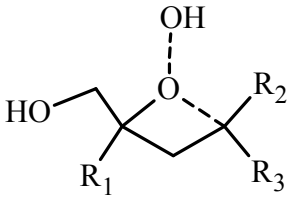
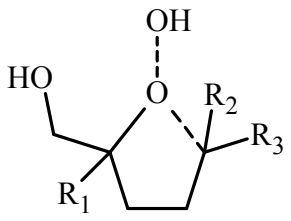
S5) Modified Arrhenius Fits of the unimolecular reactions of β-HOROO• and HOQ•OOH radicals related to reference TS

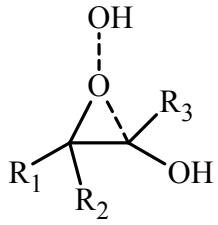
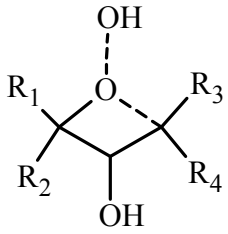
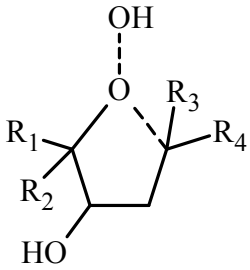
Reaction class: 1,4 H-shift of β-HOROO• radicals				
Reference TS group1	TS-substitution	$k = AT^n exp(-E/RT)$		
		A	n	E
	R_1, R_2, R_3 = H	1.35×10^{-3}	4.55	26985
	R_1 = Alkyl radical; R_2, R_3 = H	9.48×10^{-1}	3.73	26469
	R_1, R_3 = H; R_2 = Alkyl radical	2.77×10^{-1}	3.77	23992
	R_1, R_2 = Alkyl radical; R_3 = H	1.43×10^{3}	2.76	24752
	R_1 = H; R_2, R_3 = Alkyl radical;	1.52×10^{3}	2.64	22082
	R_1, R_2, R_3 = Alkyl radical	6.12×10^{3}	2.47	21089
Reference TS Group2	TS-substitution	$k = AT^n exp(-E/RT)$		
		A	n	E
	R_1, R_2, R_3 = H	9.28×10^{3}	2.46	21874
	R_1 = Alkyl radical; R_2, R_3 = H	1.76×10^{3}	2.69	21498
	R_1, R_2 = Alkyl radical; R_3 = H	1.19×10^{6}	1.94	22661
	R_1, R_2 = H; R_3 = Alkyl radical	1.92×10^{5}	2.03	20190
	R_1, R_3 = Alkyl radical; R_2 = H	2.85×10^{5}	2.00	19560
	R_1, R_2, R_3 = Alkyl radical	3.01×10^{6}	1.75	20103

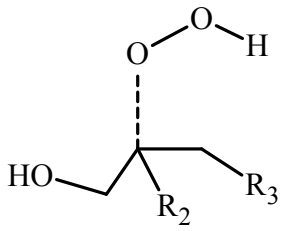
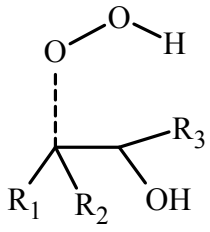
Reaction class: 1,5 H-shift of β-HOROO• radicals				
Reference TS Group1	TS-substitution	k = $AT^n exp(-E/RT)$		
		A	n	E
	R_1, R_2, R_3 = H	6.23×10^3	2.35	18430
	R_1 = Alkyl radical; R_2, R_3 = H	1.04×10^6	1.78	19403
	R_1, R_3 = H; R_2 = Alkyl radical	7.15×10^5	1.67	16221
	R_1, R_2 = Alkyl radical; R_3 = H	2.04×10^7	1.21	16239
	R_1 = H; R_2, R_3 = Alkyl radical;	4.77×10^6	1.35	13588
	R_1, R_2, R_3 = Alkyl radical	1.39×10^6	1.51	12811
Reference TS Group2	TS-substitution	k = $AT^n exp(-E/RT)$		
		A	n	E
	R_1, R_2, R_3, R_4 = H	1.53×10^5	2.05	20330
	R_1 = Alkyl radical; R_2, R_3, R_4 = H	4.12×10^4	2.20	19784
	R_1, R_2 = Alkyl radical; R_3, R_4 = H	2.22×10^6	1.81	21013
	R_1, R_2, R_4 = H; R_3 = Alkyl radical	5.76×10^6	1.54	17944
	R_1, R_3 = Alkyl radical; R_2, R_4 = H	2.34×10^7	1.41	17829
	R_1, R_2, R_3 = Alkyl radical; R_4 = H	2.27×10^9	0.83	18664
	R_1, R_2 = H; R_3, R_4 = Alkyl radical	3.86×10^7	1.21	15665
	R_1, R_3, R_4 = Alkyl radical; R_2 = H	4.42×10^8	0.97	15399
	R_1, R_2, R_3, R_4 = Alkyl radical	3.92×10^{11}	0.17	16655

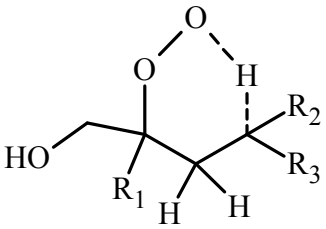
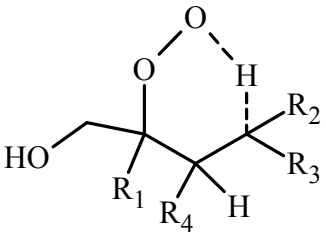
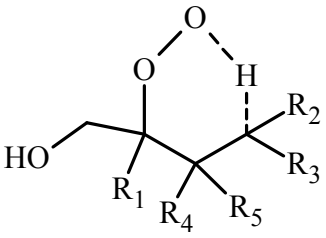
Reaction class: 1,6 H-shift of β-HOROO• radicals				
Reference TS Group1	TS-substitution	k = $AT^n exp(-E/RT)$		
		A	n	E
	R_1, R_2, R_3 = H	2.29×10^2	2.53	17005
	R_1 = Alkyl radical; R_2, R_3 = H	2.13×10^6	1.38	18485
	R_1, R_3 = H; R_2 = Alkyl radical	8.68×10^2	2.31	13600
	R_1, R_2 = Alkyl radical; R_3 = H	6.09×10^6	1.20	15177
	R_1 = H; R_2, R_3 = Alkyl radical;	2.72×10^3	2.16	11165
	R_1, R_2, R_3 = Alkyl radical	7.49×10^7	0.83	12793
Reference TS Group2	TS-substitution	k = $AT^n exp(-E/RT)$		
		A	n	E
	R_1, R_2, R_3, R_4 = H	8.48×10^5	1.59	19515
	R_1 = Alkyl radical; R_2, R_3, R_4 = H	7.43×10^6	1.34	20054
	R_1, R_2 = Alkyl radical; R_3, R_4 = H	1.82×10^9	0.68	20655
	R_1, R_2, R_4 = H; R_3 = Alkyl radical	8.36×10^6	1.26	16333
	R_1, R_3 = Alkyl radical; R_2, R_4 = H	2.64×10^7	1.16	16609
	R_1, R_2, R_3 = Alkyl radical; R_4 = H	2.44×10^9	0.62	17748
	R_1, R_2 = H; R_3, R_4 = Alkyl radical	4.56×10^9	0.40	14918
	R_1, R_3, R_4 = Alkyl radical; R_2 = H	5.25×10^{10}	0.10	15442
	R_1, R_2, R_3, R_4 = Alkyl radical	4.13×10^{12}	-0.39	16335

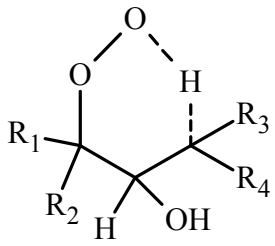
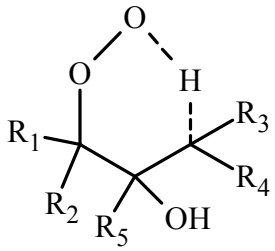
Reaction class: HO_2• elimination from β-HOROO• radicals				
Reference TS Group1	TS-substitution	$k = AT^n exp(-E/RT)$		
		A	n	E
	R_1, R_2, R_3 = H	3.86×10^{7}	1.48	29631
	R_1 = Alkyl radical; R_2, R_3 = H	3.03×10^{9}	1.22	29419
	R_1, R_3 = H; R_2 = Alkyl radical	3.15×10^{7}	1.58	28744
	R_1, R_2 = Alkyl radical; R_3 = H	3.89×10^{9}	1.07	29027
	R_1 = H; R_2, R_3 = Alkyl radical;	6.96×10^{7}	1.49	28328
	R_1, R_2, R_3 = Alkyl radical	2.38×10^{11}	0.59	29894
Reference TS Group2	TS-substitution	$k = AT^n exp(-E/RT)$		
		A	n	E
	R_1, R_2, R_3 = H	1.49×10^{13}	0.03	33209
	R_1 = Alkyl radical; R_2, R_3 = H	2.07×10^{13}	0.00	32999
	R_1, R_2 = Alkyl radical; R_3 = H	2.26×10^{16}	-0.82	33642
	R_1, R_2 = H; R_3 = Alkyl radical	3.65×10^{13}	-0.15	34790
	R_1, R_3 = Alkyl radical; R_2 = H	6.12×10^{14}	-0.47	34516
	R_1, R_2, R_3 = Alkyl radical	1.01×10^{17}	-1.01	35174

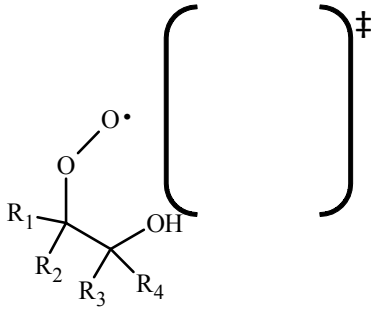
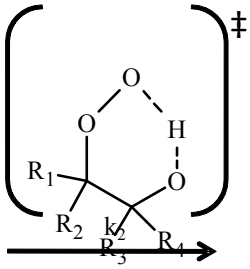
Reaction class: cyclic ether formation from β-, γ-, and δ-HOQ•OOH radicals from group 1				
Reference TS Hydroxy-oxirane	TS-substitution	$k = AT^n exp(-E/RT)$		
		A	n	E
	R_1, R_2, R_3 = H	2.26×10^{10}	0.56	10498
	R_1 = Alkyl radical; R_2, R_3 = H	4.31×10^{11}	0.10	9747
	R_1, R_3 = H; R_2 = Alkyl radical	2.76×10^{9}	1.01	8031
	R_1, R_2 = Alkyl radical; R_3 = H	2.70×10^{11}	0.11	7546
	R_1 = H; R_2, R_3 = Alkyl radical;	7.46×10^{10}	0.18	7515
	R_1, R_2, R_3 = Alkyl radical	8.35×10^{9}	0.51	7153
Reference TS Hydroxy-oxetane	TS-substitution	$k = AT^n exp(-E/RT)$		
		A	n	E
	R_1, R_2, R_3 = H	1.67×10^{11}	-0.09	16142
	R_1 = Alkyl radical; R_2, R_3 = H	3.75×10^{10}	0.13	13486
	R_1, R_3 = H; R_2 = Alkyl radical	2.44×10^{11}	-0.08	12763
	R_1, R_2 = Alkyl radical; R_3 = H	1.13×10^{11}	0.01	12001
	R_1 = H; R_2, R_3 = Alkyl radical;	8.09×10^{10}	0.08	11242
	R_1, R_2, R_3 = Alkyl radical	9.77×10^{10}	0.17	10400
Reference TS Hydroxy-oxolane	TS-substitution	$k = AT^n exp(-E/RT)$		
		A	n	E
	R_1, R_2, R_3 = H	5.02×10^{12}	-0.77	10632
	R_1 = Alkyl radical; R_2, R_3 = H	4.00×10^{12}	-0.64	9932
	R_1, R_3 = H; R_2 = Alkyl radical	7.59×10^{13}	-1.08	9093
	R_1, R_2 = Alkyl radical; R_3 = H	5.01×10^{14}	-1.30	8933
	R_1 = H; R_2, R_3 = Alkyl radical;	1.55×10^{15}	-1.42	7888
	R_1, R_2, R_3 = Alkyl radical	1.21×10^{17}	-1.92	8510

Reaction class: cyclic ether formation from β-, γ-, and δ-HOQ•OOH radicals from group 2				
Reference TS Hydroxy-oxirane	TS-substitution	$k = AT^n exp(-E/RT)$		
		A	A	A
	R_1, R_2, R_3 = H	3.11×10^{12}	0.06	11161
	R_1 = Alkyl radical; R_2, R_3 = H	3.90×10^{12}	0.02	9532
	R_1, R_2 = Alkyl radical; R_3 = H	9.88×10^{11}	0.15	7890
	R_1, R_2 = H; R_3 = Alkyl radical	8.62×10^{10}	0.56	9184
	R_1, R_3 = Alkyl radical; R_2 = H	7.44×10^{10}	0.58	7568
	R_1, R_2, R_3 = Alkyl radical	5.56×10^{13}	-0.32	7804
Reference TS Hydroxy-oxetane	TS-substitution	$k = AT^n exp(-E/RT)$		
		A	A	A
	R_1, R_2, R_3, R_4 = H	2.31×10^{15}	-1.08	21617
	R_1 = Alkyl radical; R_2, R_3, R_4 = H	1.00×10^{16}	-1.33	19882
	R_1, R_2 = Alkyl radical; R_3, R_4 = H	5.03×10^{15}	-1.21	19263
	R_1, R_2, R_4 = H; R_3 = Alkyl radical	6.83×10^{13}	-0.59	18410
	R_1, R_3 = Alkyl radical; R_2, R_4 = H	2.18×10^{14}	-0.76	17066
	R_1, R_2, R_3 = Alkyl radical; R_4 = H	3.69×10^{14}	-0.78	16261
	R_1, R_2 = H; R_3, R_4 = Alkyl radical	1.55×10^{15}	-0.88	16666
	R_1, R_3, R_4 = Alkyl radical; R_2 = H	1.95×10^{15}	-0.88	15839
	R_1, R_2, R_3, R_4 = Alkyl radical	3.09×10^{17}	-1.56	16115
Reference TS Hydroxy-oxolane	TS-substitution	$k = AT^n exp(-E/RT)$		
		A	n	E
	R_1, R_2, R_3, R_4 = H	1.93×10^{12}	-0.42	12689
	R_1 = Alkyl radical; R_2, R_3, R_4 = H	7.31×10^{11}	-0.31	12455
	R_1, R_2 = Alkyl radical; R_3, R_4 = H	1.02×10^{15}	-1.25	14452
	R_1, R_2, R_4 = H; R_3 = Alkyl radical	1.90×10^{10}	0.05	10767
	R_1, R_3 = Alkyl radical; R_2, R_4 = H	3.89×10^{11}	-0.29	10716
	R_1, R_2, R_3 = Alkyl radical; R_4 = H	1.62×10^{13}	-0.76	12015
	R_1, R_2 = H; R_3, R_4 = Alkyl radical	3.17×10^{10}	0.03	9292
	R_1, R_3, R_4 = Alkyl radical; R_2 = H	2.09×10^{11}	-0.18	9249
	R_1, R_2, R_3, R_4 = Alkyl radical	1.25×10^{12}	-0.52	8175

Reaction class: β-scission of β-HOQ•OOH radicals				
Reference TS group1	TS-substitution	$k = AT^n exp(-E/RT)$		
		A	n	E
	R_1, R_2, R_3 = H	8.17×10^{9}	0.80	14231
	R_1 = Alkyl radical; R_2, R_3 = H	5.06×10^{10}	0.54	13832
	R_1, R_3 = H; R_2 = Alkyl radical	1.97×10^{10}	0.74	14280
	R_1, R_2 = Alkyl radical; R_3 = H	1.00×10^{11}	0.48	13393
	R_1 = H; R_2, R_3 = Alkyl radical;	2.26×10^{11}	0.43	13893
	R_1, R_2, R_3 = Alkyl radical	2.66×10^{11}	0.45	13755
Reference TS Group2	TS-substitution	$k = AT^n exp(-E/RT)$		
		A	n	E
	R_1, R_2, R_3 = H	3.25×10^{12}	0.33	15980
	R_1 = Alkyl radical; R_2, R_3 = H	5.22×10^{14}	-0.24	16658
	R_1, R_2 = Alkyl radical; R_3 = H	6.39×10^{14}	-0.35	16490
	R_1, R_2 = H; R_3 = Alkyl radical	5.46×10^{10}	0.92	14881
	R_1, R_3 = Alkyl radical; R_2 = H	1.22×10^{13}	0.24	15271
	R_1, R_2, R_3 = Alkyl radical	2.23×10^{14}	-0.18	16442

Reaction class: substitution of H-atoms by alkyl groups in the cyclic part of transition states involved in the 1,5 H-shift of β-HOROO• radicals - Group 1				
Reference TS Without substitution	TS-substitution	k = $AT^n exp(-E/RT)$		
		A	n	E
	R_1, R_2, R_3 = H	6.23×10^3	2.35	18430
	R_1 = Alkyl radical; R_2, R_3 = H	1.04×10^6	1.78	19403
	R_1, R_3 = H; R_2 = Alkyl radical	7.15×10^5	1.67	16221
	R_1, R_2 = Alkyl radical; R_3 = H	2.04×10^7	1.21	16239
	R_1 = H; R_2, R_3 = Alkyl radical;	4.77×10^6	1.35	13588
	R_1, R_2, R_3 = Alkyl radical	1.39×10^6	1.51	12811
Reference TS First substitution	TS-substitution	k = $AT^n exp(-E/RT)$		
		A	n	E
	R_1, R_2, R_3 = H; R_4 = Alkyl radical	3.10×10^5	1.84	19281
	R_1, R_4 = Alkyl radical; R_2, R_3 = H	2.67×10^6	1.70	18609
	R_1, R_3 = H; R_2, R_4 = Alkyl radical	2.07×10^4	2.06	14389
	R_1, R_2, R_4 = Alkyl radical; R_3 = H	2.44×10^5	1.78	13844
	R_1 = H; R_2, R_3, R_4 = Alkyl radical;	1.56×10^6	1.50	13053
	R_1, R_2, R_3, R_4 = Alkyl radical	1.35×10^8	1.06	12964
Reference TS Second substitution	TS-substitution	k = $AT^n exp(-E/RT)$		
		A	n	E
	R_1, R_2, R_3 = H; R_4, R_5 = Alkyl radical	3.66×10^6	1.69	19284
	R_1, R_4, R_5 = Alkyl radical; R_2, R_3 = H	2.67×10^6	1.70	18609
	R_1, R_3 = H; R_2, R_4, R_5 = Alkyl radical	3.72×10^4	2.09	14706
	R_1, R_2, R_4, R_5 = Alkyl radical; R_3 = H	2.37×10^6	1.69	14313
	R_1 = H; R_2, R_3, R_4, R_5 = Alkyl radical;	3.21×10^6	1.48	12509
	R_1, R_2, R_3, R_4, R_5 = Alkyl radical	5.31×10^7	1.14	11632

Reaction class: substitution of H-atoms by alkyl groups in the cyclic part of transition states involved in the 1,5 H-shift of β-HOROO• radicals - Group 2				
Reference TS Without substitution	TS-substitution	k = $AT^n exp(-E/RT)$		
		A	n	E
	R_1, R_2, R_3, R_4 = H	1.53×10^5	2.05	20330
	R_1 = Alkyl radical; R_2, R_3, R_4 = H	4.12×10^4	2.20	19784
	R_1, R_2 = Alkyl radical; R_3, R_4 = H	2.22×10^6	1.81	21013
	R_1, R_2, R_4 = H; R_3 = Alkyl radical	5.76×10^6	1.54	17944
	R_1, R_3 = Alkyl radical; R_2, R_4 = H	2.34×10^7	1.41	17829
	R_1, R_2, R_3 = Alkyl radical; R_4 = H	2.27×10^9	0.83	18664
	R_1, R_2 = H; R_3, R_4 = Alkyl radical	3.86×10^7	1.21	15665
	R_1, R_3, R_4 = Alkyl radical; R_2 = H	4.42×10^8	0.97	15399
	R_1, R_2, R_3, R_4 = Alkyl radical	3.92×10^{11}	0.17	16655
Reference TS With substitution	TS-substitution	k = $AT^n exp(-E/RT)$		
		A	n	E
	R_1, R_2, R_3, R_4 = H; R_5 = Alkyl radical	1.01×10^7	1.46	20173
	R_1, R_5 = Alkyl radical; R_2, R_3, R_4 = H	2.11×10^5	1.96	19816
	R_1, R_2, R_5 = Alkyl radical; R_3, R_4 = H	7.22×10^5	1.90	19784
	R_1, R_2, R_4 = H; R_3, R_5 = Alkyl radical	1.66×10^5	1.87	15190
	R_1, R_3, R_5 = Alkyl radical; R_2, R_4 = H	8.48×10^4	2.11	14922
	R_1, R_2, R_3, R_5 = Alkyl radical; R_4 = H	1.07×10^6	1.73	15736
	R_1, R_2 = H; R_3, R_4, R_5 = Alkyl radical	5.42×10^8	0.78	14328
	R_1, R_3, R_4, R_5 = Alkyl radical; R_2 = H	5.97×10^7	1.17	13441
	R_1, R_2, R_3, R_4, R_5 = Alkyl radical	6.82×10^5	1.74	11660

Reaction class: Waddington mechanism of β-HOROO• radicals				
  R_1-				
TS-substitution	Reaction	$k = AT^n exp(-E/RT)$		
		A	n	E
R_1, R_2, R_3, R_4 = H	k_1	8.84×10^{10}	0.12	21163
	k_{-1}	1.28×10^{12}	-0.23	-593
	k_2	4.42×10^{15}	-0.38	9847
R_1 = Alkyl radical; R_2, R_3, R_4 = H	k_1	2.61×10^{10}	0.29	20378
	k_{-1}	8.86×10^{15}	-1.36	1500
	k_2	1.99×10^{19}	-1.50	10820
R_1, R_2 = Alkyl radical; R_3, R_4 = H	k_1	5.75×10^{13}	-0.64	21610
	k_{-1}	1.09×10^{16}	-1.41	389
	k_2	6.35×10^{18}	-1.52	8047
R_1, R_2, R_4 = H; R_3 = Alkyl radical	k_1	1.18×10^{10}	0.39	20322
	k_{-1}	4.28×10^{17}	-1.94	2592
	k_2	8.69×10^{21}	-2.37	12629
R_1, R_3 =Alkyl radical; R_2, R_4 = H	k_1	1.80×10^{11}	0.10	20330
	k_{-1}	1.22×10^{17}	-1.71	1679
	k_2	4.72×10^{20}	-2.06	9465
R_1, R_2, R_3 = Alkyl radical; R_4 = H	k_1	3.42×10^{12}	-0.22	20842
	k_{-1}	4.39×10^{18}	-2.18	1440
	k_2	1.69×10^{23}	-2.87	7744
R_1, R_2 = H; R_3, R_4 = Alkyl radical	k_1	2.14×10^{13}	-0.62	22228
	k_{-1}	7.98×10^{18}	-2.15	3826
	k_2	7.91×10^{22}	-2.61	12398
R_1, R_3, R_4 = Alkyl radical; R_2 = H	k_1	1.33×10^{11}	0.05	20310
	k_{-1}	5.80×10^{18}	-2.08	2899
	k_2	3.43×10^{22}	-2.55	10499
R_1, R_2, R_3, R_4 = Alkyl radical	k_1	4.58×10^{14}	-0.82	22410

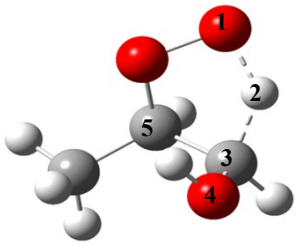
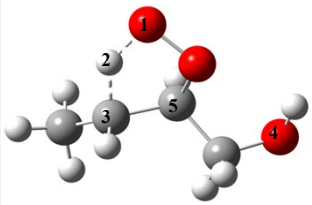
S6) Second order perturbation theory analysis of the Fock matrix in NBO basis

BD: bonding orbital, BD*: anti-bonding orbital, LP: lone pair (non-bonded orbital),

LP*: unfilled non-bonded orbital

***Table S6a**: NBO analysis for two transition state involved in the 1,4 H-shift of R_2 and R_{19} radicals (Fig. 6 of the article).*

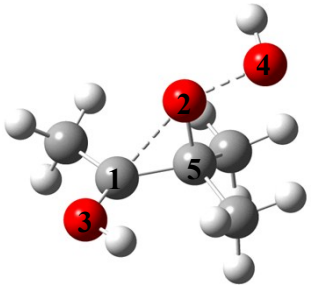
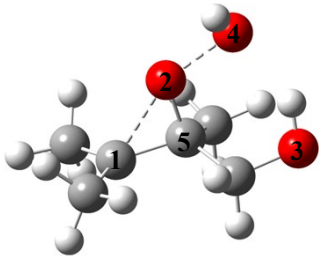
Only stabilization energy E(2) greater than 10 kcal/mol are presented in the following Table.

	Donor (i)	Occupancy	Acceptor (i)	E(2)[a] *kcal/mol*	E(j) - E(i)[b] *(a.u.)*	F(i,j)[c] *(a.u.)*
 TS R_2	α spin orbitals					
	LP (O_1)	0.9020	BD* (H_2 - C_3)	53.8	0.69	0.244
	β spin orbitals					
	BD (O_1 - H_2)	0.8178	*LP* * (C_3)	48.0	0.31	0.168
	LP (O_4)	**0.8514**	***LP*** * **(C_3)**	**34.0**	**0.24**	**0.127**
 TS R_{19}	α spin orbitals					
	LP (O_1)	0.8888	BD*(H_2 - C_3)	63.3	0.69	0.244
	β spin orbitals					
	BD (O_1 - H_2)	0.7788	*LP* * (C_3)	50.9	0.31	0.168

[a] E(2) stands for the stabilization energy. [b] energy difference between donor and acceptor (i_{th} and j_{th} NBO orbitals). [c] F(i,j) is the Fock matrix element between i_{th} and j_{th} NBO orbitals.

***Table S6b**: NBO analysis for two transition states involved in the formation of hydroxyl-oxirane, from R_6 and R_{22} radicals (Fig. 10 of the article).*

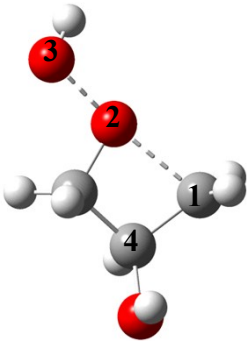
Only stabilization energy E(2) greater than 10 kcal/mol are presented in the following Table.

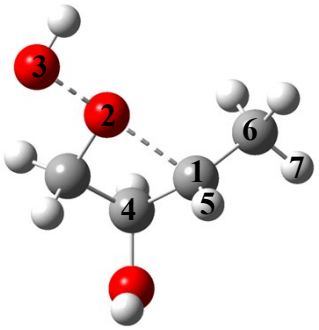
	Donor (i)	Occupancy	Acceptor (i)	E(2)[a] *kcal/mol*	E(j) - E(i)[b] *(a.u.)*	F(i,j)[c] *(a.u.)*
 TS R_6	**α spin orbitals**					
	BD (C_1 - O_2)	0.9467	BD*(C_1 - O_2)	12.2	0.12	0.056
	BD (O_2 - C_5)	0.9748	BD*(C_1 - O_2)	15.6	0.63	0.148
	LP (O_3)	**0.9503**	**BD*(C_1 - O_2)**	**16.8**	**0.22**	**0.084**
	LP (O_2)	0.9929	BD*(C_1 - O_2)	10.7	0.58	0.118
	LP (O_4)	0.7589	BD*(C_1 - O_2)	99.9	0.15	0.161
 TS R_{22}	**α spin orbitals**					
	BD (C_1 - O_2)	0.9400	BD*(C_1 - O_2)	13.3	0.14	0.061
	BD (O_2 - C_5)	0.9736	BD*(C_1 - O_2)	16.2	0.65	0.148
	LP (O_2)	0.9934	BD*(C_1 - O_2)	10.8	0.61	0.119
	LP (O_4)	0.7737	BD*(C_1 - O_2)	81.0	0.20	0.162

[a]E(2) stands for the stabilization energy. [b]energy difference between donor and acceptor (i_{th} and j_{th} NBO orbitals). [c] F(i,j) is the Fock matrix element between i_{th} and j_{th} NBO orbitals.

***Table S6C**: NBO analysis for the three transition states involved in the formation of hydroxyl-oxetane from R_4 and R_7 and R_{10} radicals (Fig. 19 of the article).*

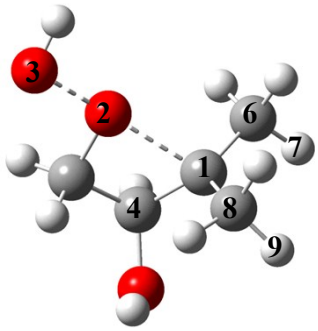
Only stabilization energy E(2) greater than 5 kcal/mol are presented in the following Table.

	Donor (i)	Occupancy	Acceptor (i)	E(2)[a] *kcal/mol*	E(j) - E(i)[b] *(a.u.)*	F(i,j)[c] *(a.u.)*
 TS R_4	α spin orbitals					
	BD (C_1 - O_2)	0.9741	BD*(C_1 - O_2)	6.7	0.21	0.054
	LP (O_2)	0.9959	BD*(C_1 - O_2)	6.7	0.67	0.097
	LP (O_3)	0.7491	BD*(C_1 - O_2)	82.6	0.22	0.171
	β spin orbitals					
	LP (O_2)	0.9302	LP*(C_1)	17.9	0.53	0.126



TS R_7

α spin orbitals					
BD (C_1 - O_2)	0.9578	BD*(C_1 - O_2)	6.9	0.20	0.052
LP (O_2)	0.9957	BD*(C_1 - O_2)	6.6	0.67	0.096
LP (O_3)	0.7527	BD*(C_1 - O_2)	80.2	0.22	0.167
Sum of all C-H σ bonds involved in the methyl group	/	**BD*(C_1-O_2)** BD*(C_1-C_4) BD*(C_1-H_5)	**2.9** 6.7	/	/
β spin orbitals					
LP (O_2)	0.94328	LP*(C_1)	14.6	0.54	0.116
BD (C_6 - H_7)	**0.96651**	**BD*(C_1-C_4)**	**7.5**	**0.45**	**0.077**
Sum of all C-H σ bonds involved in the methyl group	/	LP*(C_1) BD*(C_1-C_4) BD*(C_1-H_5)	12.8	/	/



TS R_{10}

α spin orbitals					
BD (C_1 - O_2)	0.9433	BD*(C_1 - O_2)	7.6	0.19	0.053
LP (O_2)	0.9950	BD*(C_1 - O_2)	6.8	0.66	0.098
LP (O_3)	0.7464	BD_1*(C_1 - O_2)	81.3	0.21	0.167
Sum of all C-H σ bonds involved in the methyl groups	/	**BD*(C_1-O_2)** BD*(C_1-C_4) BD*(C_1-C_6) BD*(C_1-C_8)	**6.0** 16.1	/	/
β spin orbitals					
LP (O_2)	0.9508	LP*(C_1)	13.2	0.56	0.114
BD (C_6 - H_7)	0.9675	**LP*(C_1)**	**7.7**	**0.45**	**0.079**
BD (C_8 - H_9)	0.9711	**LP*(C_1)**	**6.9**	**0.45**	**0.076**
Sum of all C-H σ bonds involved in the methyl groups	/	LP*(C_1) BD*(C_1-C_4) BD*(C_1-C_6) BD*(C_1-C_8)	27.7	/	/