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

Electronic Supporting Information for

The states that hide in the shadows: the potential role of conical intersections in the ground state unimolecular decay of a Criegee Intermediate

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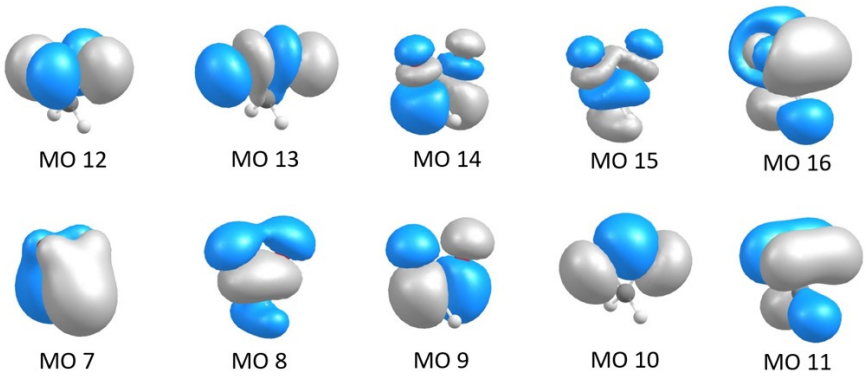
Figure S1: Active space orbitals used in the CASSCF and MS-CASPT2 calculations for dioxirane.

12/10 Active Space:



14/11 Active Space: All 12/10 orbitals above + the following occupied orbital:

6/5 Active Space used for CI optimization at the CI geometry:

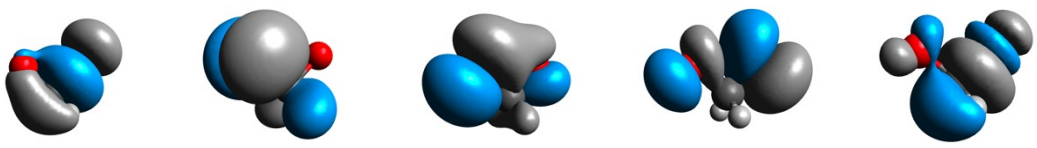
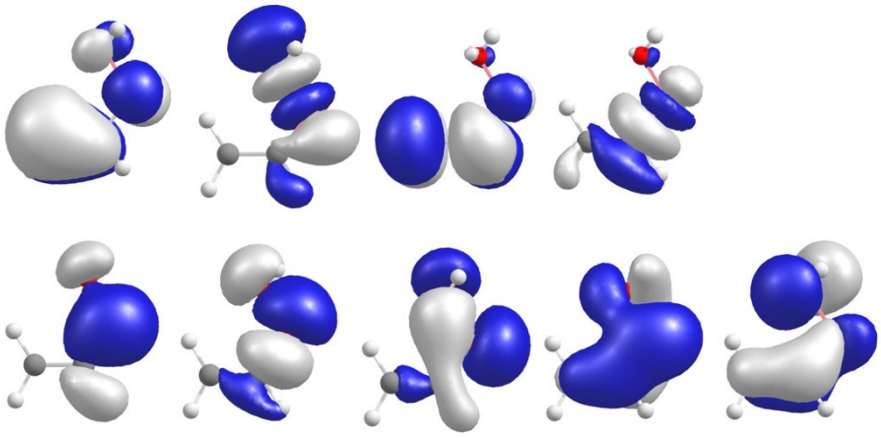
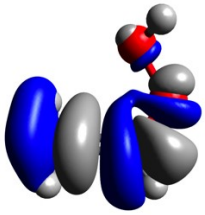


Figure S2: Active space orbitals used in the CASSCF and XMS-CASPT2 calculations for VHP.

12/9 Active Space:



12/10 Active Space: All 12/9 orbitals above + the following virtual orbital:



14/11 Active Space: All 12/9 orbitals + the following occupied (left) and virtual (right) orbitals:

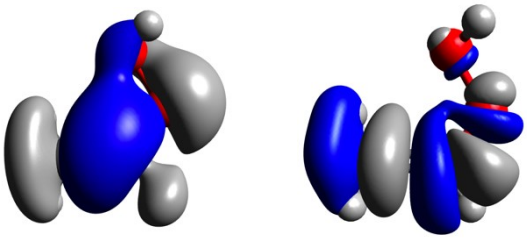


Table S1: Benchmarking the Active Space used for the CASPT2 computations in dioxirane.

	Reactant		Product	
	12/10	**14/11**	**12/10**	**14/11**
Vertical Excitation Energies / eV				
S_1-S_0	3.72	3.74	0.27	0.21
S_2-S_0	5.50	5.36	0.42	0.41
S_3-S_0	7.49	7.53	0.65	0.62

Table S2: Benchmarking the Active Space used for the CASPT2 computations in VHP.

	Reactant				Product			
	12/9	**12/10**	**14/10**	**14/11**	**12/9**	**12/10**	**14/10**	**14/11**
Vertical Excitation Energies / eV								
S_1-S_0	5.50	5.08	5.11	5.09	0.02	0.03	0.03	0.03
S_2-S_0	6.89	6.52	6.50	6.52	0.43	0.43	0.39	0.41
S_3-S_0	8.81	8.51	8.48	8.49	0.44	0.44	0.40	0.42

Cartesian Coordinates and Eigenvectors:

Ground state optimized geometry of dioxirane

SCF Energy: -189.332843639 Hartree

C	0.57612300	-0.35858500	-0.14757299
H	1.16366005	-0.85415298	0.62276202
H	0.91500098	-0.47755200	-1.17481196
O	0.06333100	0.88847798	0.18492199
O	-0.79905802	-0.35043401	0.04413300

Normal mode wavenumbers at the optimized geometry of dioxirane

		1			2			3		
		A			A			A		
Frequencies --		754.8207			902.4678			1038.8003		
Red. masses --		13.4739			9.1898			1.0962		
Frc consts --		4.5230			4.4098			0.6970		
IR Inten --		0.8479			26.5235			0.0000		
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	-0.38	0.00	0.00	-0.00	0.51	-0.00	0.00	0.00	-0.00
2	1	-0.25	-0.00	0.06	-0.00	0.44	0.00	-0.00	0.71	0.00
3	1	-0.25	0.00	-0.06	-0.00	0.44	0.00	0.00	-0.71	-0.00
4	8	0.16	0.58	0.00	0.36	-0.22	0.00	-0.00	0.00	-0.05
5	8	0.16	-0.58	-0.00	-0.36	-0.22	0.00	-0.00	-0.00	0.05
		4			5			6		
		A			A			A		
Frequencies --		1185.1795			1276.7454			1299.2953		
Red. masses --		1.2983			1.2268			5.6061		
Frc consts --		1.0745			1.1783			5.5760		
IR Inten --		7.6321			2.4206			47.9194		
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	0.00	0.00	0.15	0.00	-0.14	0.00	0.46	0.00	-0.00
2	1	-0.65	-0.00	-0.24	-0.00	0.70	0.00	0.56	-0.01	0.05
3	1	0.65	0.00	-0.24	0.00	0.70	-0.00	0.56	-0.01	-0.05
4	8	0.00	-0.00	-0.04	0.02	0.01	-0.00	-0.21	0.18	0.00
5	8	-0.00	-0.00	-0.04	-0.02	0.01	-0.00	-0.21	-0.18	-0.00
		7			8			9		
		A			A			A		

Frequencies --	1560.1156			3094.3068			3194.0122		
Red. masses --	1.1413			1.0467			1.1234		
Frc consts --	1.6366			5.9048			6.7521		
IR Inten --	3.4375			33.6338			28.4402		
Atom AN	X	Y	Z	X	Y	Z	X	Y	Z
1 6	-0.11	-0.00	-0.00	-0.06	-0.00	-0.00	0.00	0.00	-0.10
2 1	0.58	0.00	0.40	0.35	0.00	-0.61	-0.36	-0.00	0.60
3 1	0.58	0.00	-0.40	0.35	0.00	0.61	0.36	0.00	0.60
4 8	0.00	-0.01	-0.00	0.00	-0.00	0.00	0.00	-0.00	0.00
5 8	0.00	0.01	0.00	0.00	0.00	-0.00	-0.00	-0.00	0.00

Conical intersection associated with bisoxy biradical

O	-0.00044300	-0.30259800	-1.09131205
O	0.00036900	-0.26701400	1.06539595
C	0.00004800	0.60708398	0.00374600
H	-0.89420998	1.21785903	0.01060500
H	0.89423603	1.21796596	0.01157000

Derivative coupling (h) vector associated with the conical intersection

O	-0.0111914824	-0.0004419707	0.0009667999
O	0.0094458860	-0.0007826661	-0.0007095729
C	0.0024701222	0.0011570891	-0.0001143020
H	-0.0003455066	-0.0007776637	-0.0125111199
H	-0.0003790192	0.0008452114	0.0123681948

Gradient difference (g) vector associated with the conical intersection

O	0.0007578633	-0.0123314012	0.0415961962
O	-0.0006931598	-0.0364556453	-0.0226139117
C	-0.0000950511	0.0464046065	-0.0073463554
H	0.0006325706	0.0012245874	-0.0049572728
H	-0.0006022230	0.0011578526	-0.0066786563

Ground state optimized geometry of VHP

SCF Energy: -228.575662344 Hartree

C	0.00237900	-0.01993400	-0.03965500
H	0.02106100	-0.12825900	1.03493702
H	0.93215299	0.05794700	-0.58081901
C	-1.18009806	0.02265500	-0.64874798
H	-2.13482189	-0.03738900	-0.13849901
O	-1.44589996	0.15950000	-1.98256302
O	-0.20410000	0.29631701	-2.72152901
H	-0.36872900	-0.35348299	-3.41762495

Normal mode wavenumbers at the optimized geometry of dioxirane

	1	2	3
	A	A	A
Frequencies --	168.7751	240.9553	323.9731
Red. masses --	1.1055	2.2804	3.8052
Frc consts --	0.0186	0.0780	0.2353
IR Inten --	144.2510	4.7286	1.3136

Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	0.01	-0.00	0.02	-0.01	-0.00	0.10	-0.30	-0.08	-0.01
2	1	0.01	0.01	0.07	0.00	-0.00	-0.27	-0.28	-0.40	0.01
3	1	0.02	-0.00	-0.03	-0.02	-0.01	0.60	-0.59	0.07	-0.03
4	6	0.00	-0.01	0.01	0.00	0.00	-0.17	-0.03	0.10	0.00
5	1	-0.00	-0.01	0.04	0.02	-0.00	-0.66	0.10	0.04	0.02
6	8	-0.00	-0.00	-0.03	-0.00	0.00	0.20	-0.03	0.09	-0.01
7	8	-0.05	0.03	-0.04	0.00	0.01	-0.12	0.31	-0.07	0.01
8	1	0.64	-0.37	0.67	0.03	-0.20	-0.06	0.32	-0.28	0.05

	4	5	6
	A	A	A
Frequencies --	616.2186	706.5768	842.1597
Red. masses --	2.5515	1.5394	1.3510
Frc consts --	0.5708	0.4528	0.5646
IR Inten --	6.7494	5.6455	65.0558

Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	0.05	-0.08	-0.00	-0.00	0.00	0.03	0.01	0.00	-0.17
2	1	0.01	0.53	0.03	-0.02	-0.01	0.82	-0.01	-0.02	0.66
3	1	0.63	-0.35	-0.01	0.00	0.01	-0.43	-0.02	-0.01	0.73
4	6	-0.17	-0.18	-0.01	0.00	0.00	-0.20	0.00	-0.00	0.06
5	1	0.01	-0.26	0.00	-0.01	0.01	0.30	0.00	-0.00	-0.08
6	8	-0.10	0.11	-0.01	0.00	-0.00	0.08	-0.00	0.00	0.00
7	8	0.15	0.09	0.01	-0.00	-0.00	0.01	-0.00	0.00	-0.00
8	1	0.05	-0.10	-0.05	-0.03	-0.01	-0.02	0.01	-0.02	0.01

	7	8	9
	A	A	A
Frequencies --	865.9498	965.8245	968.7113
Red. masses --	8.3657	1.1941	2.1249
Frc consts --	3.6960	0.6563	1.1749
IR Inten --	25.2666	33.0444	22.6276

Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	0.10	-0.09	0.00	-0.05	0.01	0.01	-0.17	0.04	-0.01
2	1	0.11	-0.06	-0.02	-0.06	0.20	-0.29	-0.22	0.63	0.17
3	1	0.19	-0.14	0.01	0.08	-0.06	0.46	0.30	-0.17	-0.23
4	6	0.16	0.03	0.01	-0.02	0.00	-0.08	-0.06	0.01	0.05
5	1	0.57	-0.14	0.03	0.02	-0.02	0.79	0.14	-0.07	-0.45
6	8	-0.06	0.50	0.00	0.06	-0.00	0.00	0.20	-0.01	0.01
7	8	-0.18	-0.41	-0.01	-0.01	-0.02	-0.00	-0.04	-0.07	-0.01
8	1	-0.10	-0.25	0.06	0.04	0.08	0.03	0.08	0.18	0.06

	10	11	12
	A	A	A
Frequencies --	1161.4991	1327.9279	1380.3207
Red. masses --	2.6940	1.1887	1.1321
Frc consts --	2.1414	1.2350	1.2708
IR Inten --	49.6732	3.1088	34.1093

Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z

1	6	-0.10	-0.09	-0.00	0.01	0.10	0.00	0.02	0.00	0.00
2	1	-0.11	0.40	-0.01	-0.01	0.13	0.00	0.04	-0.27	0.01
3	1	0.51	-0.38	0.01	-0.32	0.26	-0.01	0.18	-0.08	-0.00
4	6	0.24	0.16	0.00	-0.01	-0.07	-0.00	-0.04	0.03	0.00
5	1	0.51	0.04	0.04	0.78	-0.43	0.02	0.19	-0.07	-0.02
6	8	-0.15	-0.10	-0.01	-0.02	-0.03	-0.00	-0.05	-0.02	0.03
7	8	-0.01	0.05	0.01	0.00	0.01	0.00	0.02	-0.03	-0.04
8	1	-0.09	-0.12	-0.04	-0.03	-0.06	-0.02	0.36	0.83	0.13

	13	14	15
	A	A	A
Frequencies --	1438.0409	1694.9001	3197.8824
Red. masses --	1.1966	4.6320	1.0582
Frc consts --	1.4579	7.8399	6.3762
IR Inten --	25.1341	135.6332	0.0461

Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	0.02	-0.06	0.00	0.20	-0.30	0.00	-0.04	0.04	-0.00
2	1	-0.03	0.66	0.01	0.20	0.35	0.01	0.71	0.05	0.01
3	1	-0.52	0.21	-0.01	-0.46	-0.05	-0.00	-0.24	-0.49	-0.01
4	6	0.08	-0.05	0.00	-0.29	0.33	-0.00	0.02	0.03	0.00
5	1	-0.27	0.10	-0.02	0.51	0.05	0.02	-0.18	-0.41	-0.00
6	8	-0.05	0.01	0.01	0.07	-0.04	-0.00	0.00	0.00	-0.00
7	8	0.01	-0.01	-0.01	-0.01	0.01	0.01	-0.00	-0.00	0.00
8	1	0.15	0.34	0.05	-0.07	-0.14	-0.01	0.00	-0.00	-0.00

	16	17	18
	A	A	A
Frequencies --	3217.0787	3303.5398	3805.6028
Red. masses --	1.0939	1.1172	1.0685
Frc consts --	6.6705	7.1836	9.1176
IR Inten --	1.9680	0.9518	70.1244

Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	-0.02	0.03	0.00	-0.08	-0.06	-0.00	-0.00	0.00	-0.00
2	1	0.31	0.02	0.01	0.62	0.04	0.01	0.00	0.00	-0.00

3	1	-0.15	-0.30	-0.01	0.32	0.70	0.02	-0.00	-0.00	-0.00
4	6	-0.02	-0.08	-0.00	-0.00	-0.01	-0.00	0.00	-0.00	-0.00
5	1	0.36	0.81	0.01	0.03	0.06	0.00	-0.00	-0.00	0.00
6	8	-0.00	-0.00	0.00	0.00	-0.00	0.00	-0.00	-0.00	0.00
7	8	0.00	0.00	0.00	-0.00	0.00	-0.00	0.04	-0.01	-0.05
8	1	0.00	0.00	-0.00	-0.00	0.00	0.00	-0.67	0.13	0.73