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Supporting Information

(Total of 11 pages)
for

A Combined Theoretical and Experimental Study on the Mechanism of *spiro*-Adamantyl-1,2-Dioxetanone Decomposition

Pooria Farahani,[*,†] Marcelo A. Oliveira,[†] Ignacio Fdez. Galván[‡,§] and Wilhelm J. Baader[*,†]

[†]*Instituto de Química, Departamento de Química Fundamental, Universidade de São Paulo, C.P. 05508-000, São Paulo, SP, Brazil*
[‡]*Department of Chemistry – Ångström, Uppsala University, P.O. Box 518, SE-751 20 Uppsala, Sweden,*
[§]*Uppsala Center for Computational Chemistry, Uppsala University, P.O. Box 518, SE-751 20 Uppsala, Sweden*

E-mail: wjbaader@iq.usp.br; fpooria@iq.usp.br

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[*] To whom correspondence should be addressed
[†] São Paulo
[‡] Uppsala
[§] UC_3

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Table S1. Cartesian coordinates (in Å) of the optimized *spiro*-adamantyl-1,2-dioxetanone structures at the MS-CASPT2/ANO-L-VDZP level of theory.

Reactant:

C	-1.73343029	1.31749906	0.26622410
C	-0.55005144	1.37895995	-0.70393947
C	0.70225032	1.13217885	0.13506309
C	0.71029738	-0.27738875	0.72340421
C	0.53816449	-1.33254839	-0.38959049
C	-0.77897447	-1.09114116	-1.13705049
H	0.54258390	-2.32346776	0.06834031
H	1.37303944	-1.30371886	-1.09133825
C	-1.95888936	-1.14193294	-0.15412996
C	-1.77838324	-0.07015906	0.93022060
H	-2.01978256	-2.13059428	0.30527787
H	-2.89699960	-0.97774132	-0.68817524
H	-2.65832493	1.50885114	-0.27808886
H	-1.62518642	2.10254517	1.01382424
C	-0.69927452	0.29371142	-1.79100719
H	-0.48020260	2.36115111	-1.17261975
H	-1.60528415	0.49929901	-2.36417719
H	0.13449107	0.32401591	-2.49401050
H	-0.91101162	-1.85491591	-1.90677833
C	-0.47114369	-0.34140095	1.69576750
H	1.65389721	-0.44347640	1.24424288
H	-0.50180237	-1.32525811	2.16417958
H	-0.32459070	0.39329374	2.48675786
H	-2.61291943	-0.10140480	1.63086051
C	1.99743721	1.57855268	-0.49062569
O	2.21688126	2.56784250	0.46373415
O	0.91102067	2.17341597	1.15902481
O	2.69853843	1.30674221	-1.42524030

TS_{S0} :

C	-1.78874585	1.29372132	0.32902745
C	-0.58911058	1.43358238	-0.61855466
C	0.69353981	1.19889219	0.20811815
C	0.70937518	-0.22288117	0.80206234
C	0.60628740	-1.26173564	-0.32447637
C	-0.68311303	-1.02012828	-1.12488877
H	0.58735396	-2.25491740	0.12548964
H	1.47426557	-1.21739582	-0.97282038
C	-1.89082122	-1.15390938	-0.18718724
C	-1.79259748	-0.11606966	0.94114928

H	-1.92213372	-2.15984553	0.23431048
H	-2.81490614	-1.00517735	-0.74829329
H	-2.70400979	1.46101063	-0.23941398
H	-1.74801206	2.05183809	1.10853441
C	-0.67262045	0.38877322	-1.73875889
H	-0.55003159	2.44203939	-1.03619289
H	-1.58940172	0.56269235	-2.30287852
H	0.15634694	0.49794967	-2.43150859
H	-0.74794581	-1.75629447	-1.92712651
C	-0.49953455	-0.35213740	1.73915157
H	1.63867078	-0.35772094	1.36044576
H	-0.50139558	-1.35396011	2.16981255
H	-0.42046237	0.35502217	2.56228354
H	-2.64812732	-0.21309891	1.61073872
C	1.94228831	1.46526319	-0.66896466
O	2.57823293	2.57987651	-0.29657527
O	0.67991803	2.12300032	1.23643971
O	2.36904032	0.81452063	-1.60977361

TS_{S0}^{C-C}:

C	-1.75470327	1.32243876	0.39431412
C	-0.54498509	1.48338964	-0.54651518
C	0.71415804	1.17005319	0.27842109
C	0.68210044	-0.29133730	0.76356310
C	0.53933021	-1.24555336	-0.43143312
C	-0.75421433	-0.93780116	-1.19995892
H	0.52526618	-2.27259856	-0.06338302
H	1.40253937	-1.16350313	-1.09403039
C	-1.96153243	-1.09360289	-0.26473548
C	-1.82479779	-0.12162551	0.91603084
H	-2.02250126	-2.12025584	0.10244456
H	-2.88500505	-0.89343292	-0.81213337
H	-2.66555798	1.57290111	-0.15140024
H	-1.67784019	2.02226636	1.22726482
C	-0.69795164	0.50413438	-1.72326402
H	-0.49194423	2.51130608	-0.90438419
H	-1.61721581	0.74467532	-2.25975907
H	0.11824947	0.61529924	-2.43512139
H	-0.84829946	-1.62520244	-2.04262500
C	-0.53777494	-0.44275921	1.69026820
H	1.59932283	-0.49122209	1.31199442
H	-0.57083072	-1.46479155	2.07093609
H	-0.43589091	0.21706992	2.55261644

H	-2.68452937	-0.22506641	1.58064466
C	2.15589373	1.41204690	-0.49471139
O	1.97812401	2.06740155	-1.59911697
O	0.89857618	2.04367317	1.30573630
O	3.17834710	1.03850056	-0.02513088

TS^{C-C}_{S1} :

C	-1.80562566	1.29294002	0.30734491
C	-0.57114919	1.44904334	-0.61081380
C	0.66680034	1.22127313	0.27310217
C	0.69221109	-0.21527533	0.82316212
C	0.59197233	-1.25217627	-0.30847853
C	-0.68655811	-1.01283852	-1.12649134
H	0.55775135	-2.24236523	0.14885108
H	1.46540242	-1.21913610	-0.94884495
C	-1.91260082	-1.15626376	-0.21472967
C	-1.82822466	-0.11987676	0.91413816
H	-1.95408758	-2.16390632	0.20402445
H	-2.82900865	-1.00953781	-0.79015402
H	-2.70186085	1.45483695	-0.29301482
H	-1.79966704	2.04612334	1.09217439
C	-0.65885871	0.39940139	-1.73171290
H	-0.54062189	2.45605127	-1.02810084
H	-1.57991476	0.58113576	-2.28794853
H	0.16634893	0.49889486	-2.42741734
H	-0.73754480	-1.74634709	-1.93290735
C	-0.54949696	-0.36159269	1.73366896
H	1.60222798	-0.36688499	1.40450316
H	-0.55575721	-1.37221735	2.14409012
H	-0.49665243	0.32935250	2.57215812
H	-2.69633603	-0.21433281	1.56922361
C	2.21458888	1.53220242	-0.74022441
O	2.73948512	2.47943497	-0.16961790
O	0.67836030	2.11196005	1.30144030
O	2.38444798	0.81914151	-1.66700313

TS^{C-C}_{T1} :

C	-1.80646585	1.29272179	0.30761467
C	-0.57233932	1.44981725	-0.60985061
C	0.66967506	1.22532136	0.27408154
C	0.69142884	-0.21415076	0.82464058
C	0.59261914	-1.25015825	-0.30784934
C	-0.68623222	-1.01208860	-1.12568712

H	0.56083300	-2.24099297	0.14826947
H	1.46561496	-1.21457733	-0.94872946
C	-1.91238117	-1.15633143	-0.21429300
C	-1.82887614	-0.11991545	0.91459424
H	-1.95338516	-2.16406787	0.20431483
H	-2.82864743	-1.01016185	-0.79010172
H	-2.70243570	1.45362369	-0.29346698
H	-1.80204234	2.04613318	1.09224785
C	-0.65855709	0.40014175	-1.73077274
H	-0.54313266	2.45655626	-1.02771534
H	-1.57868188	0.58180145	-2.28858781
H	0.16775658	0.49942527	-2.42509007
H	-0.73674447	-1.74563779	-1.93210581
C	-0.55017260	-0.36116243	1.73403990
H	1.60100393	-0.36646677	1.40636805
H	-0.55610712	-1.37214985	2.14367089
H	-0.49793441	0.32898476	2.57323549
H	-2.69708138	-0.21463631	1.56951135
C	2.20871756	1.52616735	-0.74022447
O	2.74910992	2.46970750	-0.17231979
O	0.67594923	2.11058827	1.29967115
O	2.38414012	0.82054826	-1.67504371

Table S2. Energies (in kcal/mol) of the low-lying singlet and triplet states at the optimized transition states geometries of spiro-adamantyl-1,2-dioxetanone relative to the ground-state energy of the reactant (React). The energies are at MS-CASPT2/ANO-L-VTZP//MS-CASPT2/ANO-L-VDZP.

	REAC	TS_OO_S0	TS_CC_S0	TS_CC_T1	TS_CC_S1
S0	0.00	30.98	23.95	9.71	8.67
S1	91.49	32.88	34.59	26.28	26.12
S2	133.31	47.75	50.92	73.51	75.05
T1	68.59	30.09		23.80	23.52
T2	127.45	35.20		37.13	36.69

Table S3. Zero-point vibrational energies (in kcal/mol) of the low-lying singlet and triplet states at the optimized transition states geometries of *spiro*-adamntyl-1,2-dioxetanone relative to the ground-state energy of the reactant (React).

	REAC	TS_OO_S0	TS_CC_S0	TS_CC_T1	TS_CC_S1
S0	0.00	29.98	21.97	7.73	6.69
S1	91.49	31.88	32.61	24.30	24.14
S2	133.31	46.75	48.94	71.53	73.07
T1	68.59	29.09		21.82	21.54
T2	127.45	34.20		35.15	34.71

Table S4. Gibbs free energies (in kcal/mol) of the low-lying singlet and triplet states at the optimized geometries of *spiro*-adamantyl-1,2-dioxetanone relative to the ground-state energy of the reactant (React).

	REAC	TS_OO_S0	TS_CC_S0	TS_CC_T1	TS_CC_S1
S0	0.00	30.43	22.11	7.87	6.83
S1	91.49	32.33	32.75	24.44	24.28
S2	133.31	47.20	49.08	71.67	73.21
T1	68.59	29.54		21.96	21.68
T2	127.45	34.65		35.29	34.85

Table S5. Spin-orbit interactions (cm^{-1}) of the main transition states computed at the MS-CASPT2(16in13)/ ANO-L-VTZP.

State 1	State 2	$\lvert\langle \Psi_1 \rvert H_{SO} \rvert \Psi_2 \rangle\rvert$ (cm^{-1})			
		TS^{O-O}_{S0}	TS^{C-C}_{S0}	TS^{C-C}_{S1}	TS^{C-C}_{T1}
$T_1(M_s=-1)$	$S_0(M_s=0)$	1.351	31.332	31.945	31.659
$T_1(M_s=0)$	$S_0(M_s=0)$	1.727	52.262	50.194	50.154
$T_1(M_s=1)$	$S_0(M_s=0)$	1.351	31.332	31.945	31.659
$T_2(M_s=-1)$	$S_0(M_s=0)$	32.496	1.809	8.019	7.719
$T_2(M_s=0)$	$S_0(M_s=0)$	51.045	1.251	6.766	6.777
$T_2(M_s=1)$	$S_0(M_s=0)$	32.496	1.809	8.019	7.719
$T_1(M_s=-1)$	$S_1(M_s=0)$	32.660	1.103	1.428	1.460
$T_1(M_s=0)$	$S_1(M_s=0)$	50.909	<1.000	<1.000	1.053
$T_1(M_s=1)$	$S_1(M_s=0)$	31.660	1.103	1.428	1.460
$T_2(M_s=-1)$	$S_1(M_s=0)$	2.559	32.980	28.882	28.841
$T_2(M_s=0)$	$S_1(M_s=0)$	1.230	45.208	48.730	48.825
$T_2(M_s=1)$	$S_1(M_s=0)$	2.559	32.980	28.882	28.841
$T_1(M_s=-1)$	$S_2(M_s=0)$	42.314	3.770	<1.000	<1.000
$T_1(M_s=0)$	$S_2(M_s=0)$	15.666	12.947	<1.000	<1.000
$T_1(M_s=1)$	$S_2(M_s=0)$	42.314	3.770	<1.000	<1.000
$T_2(M_s=-1)$	$S_2(M_s=0)$	<1.000	21.748	31.712	32.527
$T_2(M_s=0)$	$S_2(M_s=0)$	<1.000	53.951	34.357	34.735
$T_2(M_s=1)$	$S_2(M_s=0)$	<1.000	21.748	31.712	32.527
$T_2(M_s=-1)$	$T_1(M_s=-1)$	50.858	44.640	48.362	48.518
$T_2(M_s=0)$	$T_1(M_s=-1)$	32.376	33.031	28.584	28.581
$T_2(M_s=1)$	$T_1(M_s=0)$	32.376	33.031	28.584	28.581
$T_2(M_s=-1)$	$T_1(M_s=0)$	32.376	33.031	28.584	28.581
$T_2(M_s=0)$	$T_1(M_s=1)$	32.376	33.031	28.583	28.581
$T_2(M_s=1)$	$T_1(M_s=1)$	50.858	44.640	48.362	48.518

Fig. S1. The minimum energy path of the first triplet state computed CASPT2/ANO-L-VTZP//CASSCF/ANO-L-VDZP.

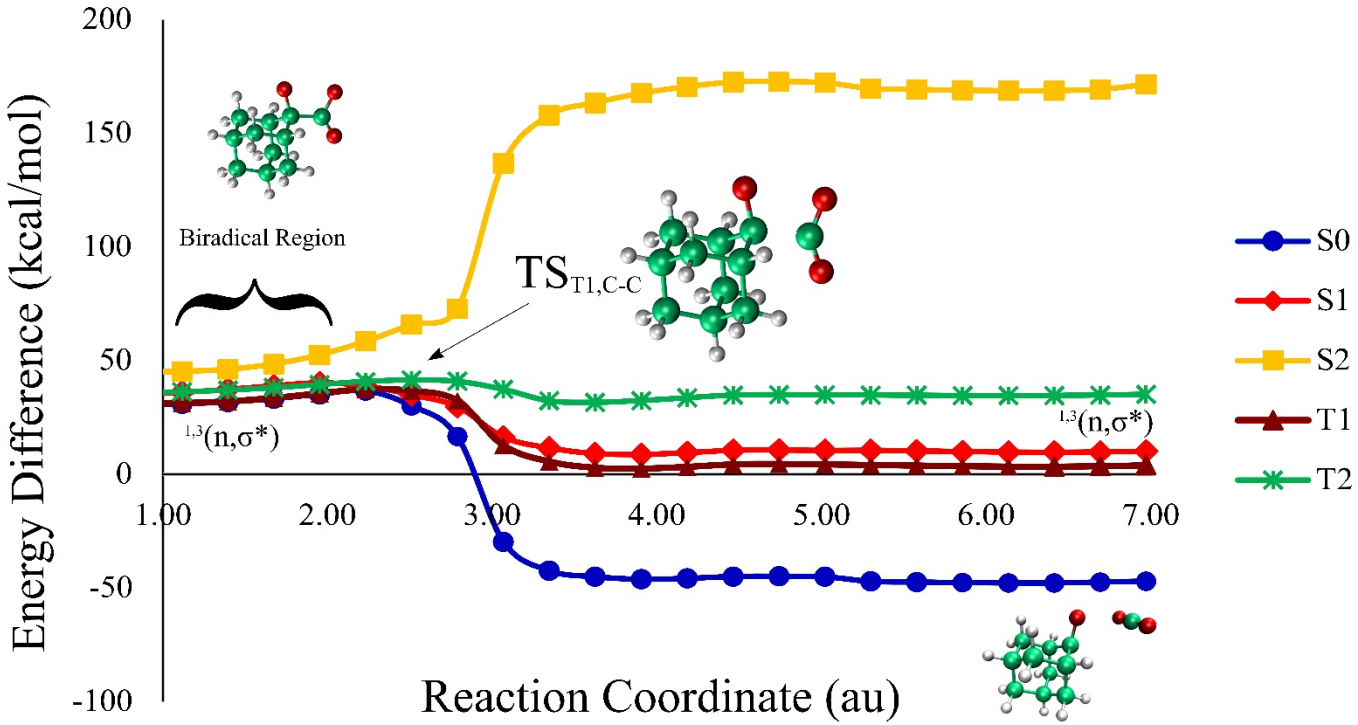

Fig. S2. Pseudo-natural (average) orbitals of the important transition state geometries optimized at the SA-CASSCF(16in13)/ANO-L-VTZP.