Supporting Information

Is the Mechanism of the [2+2] Cycloaddition of Cyclopentyne to Ethylene Concerted or Biradical? A Completely Renormalized Coupled Cluster Study

Armağan KINAL and Piotr PIECUCH

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824

The electronic energies of all species calculated with the (U)B3LYP, CCSD(T) and CR-CCSD(T) methods are given in Table S1. The geometries optimized with the (U)B3LYP/6-311G(d,p) approach, used in the (U)B3LYP, CCSD(T), and CR-CCSD(T) calculations with the 6-311G(d,p) and 6-311++G(2d,2p) basis sets (Table S1, parts (b) and (c)), and the corresponding ZPVE and thermal corrections can be found in the supporting information for Ref. 12. The CCSD(T) and CR-CCSD(T) energies of the reactants and transition states **ab**‡ and **ac**‡, optimized at the (U)MP2/6-311G(d,p) level, are given in Table S2. The geometries of all species optimized with the (U)B3LYP/6-31G(d) approach, used in the (U)B3LYP, CCSD(T), and CR-CCSD(T) calculations employing the 6-31G(d) basis set (Table S1, part (a)), and the geometries of the reactants and transition states **ab**‡ and **ac**‡, optimized at the (U)MP2/6-311G(d,p) level, are provided below Table S2.

Table S1. Electronic energies (in hartrees) of all species pertaining to the biradical and concerted pathways of the [2+2] cycloaddition of cyclopentyne to ethylene obtained with the (U)B3LYP, CCSD(T), and CR-CCSD(T) methods and (a) 6-31G(d), (b) 6-311G(d,p), and (c) 6-311++G(2d,2p) basis sets. The energy calculations with the 6-31G(d) basis set employed the geometries obtained in the (U)B3LYP/6-31G(d) geometry optimizations (see the later part of this document). The energy calculations with the 6-311G(d,p) and 6-311++G(2d,2p) basis sets employed the geometries obtained in the (U)B3LYP/6-311G(d,p) geometry optimizations reported in Ref. 12.

(a)		**(U)B3LYP**	**CCSD(T)**	**CR-CCSD(T)**
6-31G(d)	**reactants**	-272.5528211	-271.6807519	-271.6646696
	ab‡	-272.5501108	-271.6743461	-271.6555694
	b	-272.5988639	-272.0352612	-271.6920737
	bp‡	-272.5965030	-271.7854863	-271.6831506
	bc‡	-272.5835735	-271.6939312	-271.6769372
	ac‡	-272.5523422	-271.6700600	-271.6549709
	c	-272.6178297	-271.7377184	-271.7259353
	cp‡	-272.6093549	-271.7285108	-271.7160110
	p	-272.6985706	-271.8185482	-271.8064129

(b)		**(U)B3LYP**	**CCSD(T)**	**CR-CCSD(T)**
6-311G(d,p)	**reactants**	-272.6321677	-271.8694428	-271.8497758
	ab‡	-272.6268616	-271.8620555	-271.8388311
	b	-272.6708083	-272.3353757	-271.8749071
	bp‡	-272.6684660	-271.9738187	-271.8621003
	bc‡	-272.6561854	-271.8839702	-271.8626759
	ac‡	-272.6294902	-271.8600230	-271.8407245
	c	-272.6902172	-271.9273346	-271.9116486
	cp‡	-272.6811635	-271.9190296	-271.9025182
	p	-272.7671142	-272.0045239	-271.9885611

(c)		(U)B3LYP	CCSD(T)	CR-CCSD(T)
6-311++G(2d,2p)	**reactants**	-272.6481710	-271.9397341	-271.9174910
	ab‡	-272.6417960	-271.9330909	-271.9071158
	b	-272.6846847	-272.5161508	-271.9421782
	bp‡	-272.6824819	-272.0309565	-271.9244126
	bc‡	-272.6704897	-271.9532523	-271.9297384
	ac‡	-272.6451439	-271.9313187	-271.9094482
	c	-272.7038618	-271.9932324	-271.9750861
	cp‡	-272.6949485	-271.9855103	-271.9665462
	p	-272.7796708	-272.0702625	-272.0519267

Table S2. The CCSD(T) and CR-CCSD(T) energies (in hartrees) of the reactants and transition states **ab**‡ and **ac**‡ optimized at the (U)MP2/6-311G(d,p) level of theory.

	reactants	**ab**‡	**ac**‡
CCSD(T)/6-311++G(2d,2p)//(U)MP2/6-311G(d,p)	-271.9396395	-271.9323733	-271.9298516
CR-CCSD(T)/6-311++G(2d,2p)//(U)MP2/6-311G(d,p)	-271.9168237	-271.9072170	-271.9088987

In the following, all energies are in hartrees and Cartesian coordinates are in Å. Thermodynamic calculations were performed with unscaled frequencies at 298 K.

The UB3LYP/6-31G(d) optimized structure of **cyclopentyne, a**

ATOM	X	Y	Z
C	0.255784	1.092827	0.000000
C	-0.075190	0.204070	1.269185
C	-0.075190	-1.159690	-0.624319
C	-0.075190	0.204070	-1.269185
C	-0.075190	-1.159690	0.624319
H	1.329331	1.311806	0.000000
H	-0.268511	2.056604	0.000000
H	-1.059354	0.435787	1.694966
H	0.663876	0.335246	2.066405
H	0.663876	0.335246	-2.066405
H	-1.059354	0.435787	-1.694966

E(UBLYP) = -193.965362818
Detailed UB3LYP results:
Sum of electronic and zero-point energies= -193.873698
Sum of electronic and thermal energies= -193.868871
Sum of electronic and thermal enthalpies= -193.867927
Sum of electronic and thermal free energies= -193.901102

The RB3LYP/6-31G(d) optimized structure of **ethylene**

ATOM	X	Y	Z
C	0.000000	0.000000	0.665490
C	0.000000	0.000000	-0.665490
H	0.000000	0.923657	-1.239497
H	0.000000	-0.923657	-1.239497
H	0.000000	-0.923657	1.239497
H	0.000000	0.923657	1.239497

E(RB3LYP) = -78.5874582913
Detailed RB3LYP results:
Sum of electronic and zero-point energies= -78.536231
Sum of electronic and thermal energies= -78.533189
Sum of electronic and thermal enthalpies= -78.532245
Sum of electronic and thermal free energies= -78.557106

The UB3LYP/6-31G(d) optimized structure of transition state **ab**‡

ATOM	X	Y	Z
C	-0.081791	-0.246198	0.133782

C	-2.362186	-0.458824	0.460463
C	-2.941830	0.286208	-0.509055
C	0.689871	-1.209134	-0.113404
C	2.145663	-0.784505	-0.108579
C	2.005675	0.786207	-0.176018
C	0.537606	1.112399	0.301880
H	2.639913	-1.113565	0.814748
H	2.733349	-1.180590	-0.944169
H	2.774275	1.313980	0.402049
H	2.113131	1.105332	-1.218932
H	0.505673	1.439539	1.350444
H	0.069748	1.902210	-0.297019
H	-2.256966	-1.532966	0.354000
H	-2.222082	-0.064419	1.463187
H	-3.182552	-0.134538	-1.481383
H	-3.132536	1.348091	-0.377341

E(UB3LYP) = -272.550110772
Detailed UB3LYP results:
Sum of electronic and zero-point energies= -272.406135
Sum of electronic and thermal energies= -272.397736
Sum of electronic and thermal enthalpies= -272.396791
Sum of electronic and thermal free energies= -272.440051

The UB3LYP/6-31G(d) optimized structure of intermediate **b**

ATOM	X	Y	Z
C	0.322924	-0.281018	-0.216607
C	1.804410	-0.456694	-0.424100
C	2.641494	0.287410	0.570620
C	-0.596725	-1.187918	0.083831
C	-2.017597	-0.731187	0.176528
C	-1.811002	0.820377	0.184768
C	-0.382132	1.068460	-0.379160
H	-2.602295	-1.067650	-0.691352
H	-2.540854	-1.086816	1.071479
H	-2.587038	1.344655	-0.381930
H	-1.860976	1.177492	1.218763
H	-0.405662	1.352106	-1.442559
H	0.139422	1.876402	0.149189
H	2.036160	-1.536018	-0.389404
H	2.074581	-0.131131	-1.441008
H	2.325372	0.358987	1.606832
H	3.653062	0.595393	0.324717

E(UB3LYP) = -272.598863940
Detailed UB3LYP results:
Sum of electronic and zero-point energies= -272.452594
Sum of electronic and thermal energies= -272.444778
Sum of electronic and thermal enthalpies= -272.443834
Sum of electronic and thermal free energies= -272.484672

The UB3LYP/6-31G(d) optimized structure of transition state **bp**‡

ATOM	X	Y	Z
C	0.342526	0.067272	-0.257678
C	-0.343848	-1.066765	-0.286541
C	-1.824889	-0.988493	-0.098395
C	-1.965394	0.487639	0.402428
C	-0.647075	1.207739	-0.003063
C	1.823335	0.292625	-0.457830
C	2.680293	-0.379127	0.567966
H	-2.055488	0.483700	1.493692
H	-2.857364	0.978758	0.000604
H	-2.357243	-1.157832	-1.045163
H	-2.220508	-1.712080	0.623618
H	-0.773102	1.809092	-0.916439
H	-0.294489	1.895017	0.777501
H	2.108096	-0.055539	-1.468486
H	2.033905	1.373170	-0.469895
H	3.741252	-0.154645	0.627448
H	2.285256	-1.184968	1.175796

E(UB3LYP) = -272.596503018
Detailed UB3LYP results:
Sum of electronic and zero-point energies= -272.450594
Sum of electronic and thermal energies= -272.443478
Sum of electronic and thermal enthalpies= -272.442534
Sum of electronic and thermal free energies= -272.481732

The UB3LYP/6-31G(d) optimized structure of transition state **bc**‡

ATOM	X	Y	Z
C	0.408472	-0.124710	-0.277537
C	1.882081	-0.124084	-0.634824
C	2.197924	0.023311	0.794447
C	-0.343632	-1.218773	0.031515
C	-1.806623	-0.855722	-0.008358
C	-1.782422	0.671697	0.305842
C	-0.426378	1.153967	-0.263934
H	-2.217657	-1.041295	-1.014286
H	-2.426407	-1.424292	0.694749
H	-2.641388	1.210719	-0.107755
H	-1.795769	0.811669	1.392861
H	-0.537878	1.500608	-1.304168
H	0.006716	1.987880	0.301377
H	2.215597	-1.063859	-1.076647
H	2.164002	0.722505	-1.266265
H	2.277918	-0.853744	1.424197
H	2.178337	0.995698	1.273028

E(UB3LYP) = -272.583573507

Detailed UB3LYP results:
Sum of electronic and zero-point energies= -272.437302
Sum of electronic and thermal energies= -272.430631
Sum of electronic and thermal enthalpies= -272.429687
Sum of electronic and thermal free energies= -272.467598

The RB3LYP/6-31G(d) optimized structure of transition state **ac**‡

ATOM	X	Y	Z
C	0.048070	-0.153944	0.014181
C	2.492893	-0.047820	-0.649652
C	2.458467	-0.018934	0.692543
C	-0.442507	-1.317640	0.023885
C	-1.937987	-0.873022	-0.057020
C	-2.003761	0.703828	0.112555
C	-0.526157	1.204242	-0.113220
H	-2.325998	-1.182164	-1.034990
H	-2.544663	-1.378262	0.702375
H	-2.716547	1.186343	-0.566144
H	-2.306825	0.952122	1.135199
H	-0.374500	1.650474	-1.104254
H	-0.202687	1.929157	0.640864
H	2.467126	-0.984511	-1.196541
H	2.559039	0.862482	-1.240223
H	2.409542	-0.931241	1.277454
H	2.501414	0.915343	1.246626

E(RB3LYP) = -272.552342217
Detailed RB3LYP results:
Sum of electronic and zero-point energies= -272.407780
Sum of electronic and thermal energies= -272.399382
Sum of electronic and thermal enthalpies= -272.398438
Sum of electronic and thermal free energies= -272.441078

The RB3LYP/6-31G(d) optimized structure of carbene intermediate **c**

ATOM	X	Y	Z
C	0.507899	-0.026135	-0.209332
C	-0.191214	-1.292161	-0.176223
C	-1.634734	-0.879790	-0.080141
C	-1.735031	0.623770	0.295002
C	-0.418864	1.197943	-0.262425
C	1.989682	0.028738	-0.550186
C	1.645147	-0.102062	0.881250
H	-1.974873	-1.038625	-1.124022
H	-2.252366	-1.554487	0.524523
H	-2.628125	1.119783	-0.100073
H	-1.760562	0.725045	1.387515
H	-0.545604	1.515935	-1.306905
H	-0.047020	2.065251	0.295543
H	2.399112	-0.839264	-1.056851

H	2.351415	0.991214	-0.902872
H	1.789956	-1.058208	1.369965
H	1.690755	0.771546	1.525507

E(RB3LYP) = -272.617829683
Detailed RB3LYP results:
Sum of electronic and zero-point energies= -272.468836
Sum of electronic and thermal energies= -272.462273
Sum of electronic and thermal enthalpies= -272.461329
Sum of electronic and thermal free energies= -272.499165

The RB3LYP/6-31G(d) optimized structure of transition state **cp**‡

ATOM	X	Y	Z
C	0.510195	0.239056	-0.464684
C	0.046709	-1.082590	-0.541954
C	-1.431376	-0.972080	-0.182796
C	-1.713000	0.448025	0.399567
C	-0.531398	1.298634	-0.114022
C	1.974036	0.364101	-0.243045
C	1.362464	-0.583462	0.773631
H	-1.970918	-1.117752	-1.131439
H	-1.773780	-1.779566	0.474682
H	-2.688439	0.853061	0.109556
H	-1.695539	0.414810	1.496112
H	-0.782983	1.846167	-1.033563
H	-0.169278	2.043252	0.605065
H	2.628209	-0.115300	-0.966266
H	2.338213	1.324000	0.117874
H	1.748594	-1.590759	0.842763
H	1.060142	-0.148015	1.725038

E(RB3LYP) = -272.609354934
Detailed RB3LYP results:
Sum of electronic and zero-point energies= -272.460541
Sum of electronic and thermal energies= -272.454518
Sum of electronic and thermal enthalpies= -272.453573
Sum of electronic and thermal free energies= -272.490086

The RB3LYP/6-31G(d) optimized structure of product **p**

ATOM	X	Y	Z
C	0.306515	0.665327	-0.008985
C	0.306515	-0.665328	-0.008985
C	-1.059900	-1.280266	0.070848
C	-1.962706	0.000000	-0.104899
C	-1.059899	1.280267	0.070846
C	1.825602	0.792256	-0.016953
C	1.825601	-0.792256	-0.016955
H	-1.267352	-2.031368	-0.702268

H	-1.234237	-1.774331	1.037943
H	-2.389796	-0.000001	-1.113193
H	-2.802721	0.000001	0.596738
H	-1.267350	2.031366	-0.702272
H	-1.234238	1.774335	1.037939
H	2.273220	1.254005	-0.905747
H	2.279439	1.244843	0.873564
H	2.273212	-1.253997	-0.905759
H	2.279446	-1.244852	0.873553

E(RB3LYP) = -272.698570579
Detailed RB3LYP results:
Sum of electronic and zero-point energies= -272.546761
Sum of electronic and thermal energies= -272.540463
Sum of electronic and thermal enthalpies= -272.539519
Sum of electronic and thermal free energies= -272.576986

The RMP2/6-311G(d,p) optimized structure of **cyclopentyne**, **a**

ATOM	X	Y	Z
C	-1.184072	-0.153655	0.000000
C	-0.273781	0.126489	1.254978
C	-0.273781	0.126489	-1.254978
C	1.067601	-0.148083	-0.626679
C	1.067601	-0.148083	0.626679
H	-1.421573	-1.222734	0.000000
H	-2.131371	0.399619	0.000000
H	-0.328678	1.172323	1.576759
H	-0.328678	1.172323	-1.576759
H	-0.534627	-0.507184	2.106147
H	-0.534627	-0.507184	-2.106147

E(RMP2) = -193.421344349
Detailed RMP2 results:
Sum of electronic and zero-point energies= -193.325813
Sum of electronic and thermal energies= -193.321622
Sum of electronic and thermal enthalpies= -193.320678
Sum of electronic and thermal free energies= -193.352649

The RMP2/6-311G(d,p) optimized structure of **ethylene**

ATOM	X	Y	Z
C	0.000000	-0.668165	0.000000
C	0.000000	0.668165	0.000000
H	-0.925952	1.233469	0.000000
H	0.925952	1.233469	0.000000
H	-0.925952	-1.233469	0.000000
H	0.925952	-1.233469	0.000000

E(RMP2) = -78.347294648
Detailed RMP2 results:
Sum of electronic and zero-point energies= -78.295855
Sum of electronic and thermal energies= -78.292805
Sum of electronic and thermal enthalpies= -78.291860
Sum of electronic and thermal free energies= -78.316736

The UMP2/6-311G(d,p) optimized structure of transition state **ab**‡

ATOM	X	Y	Z
C	0.101733	0.237341	0.218085
C	2.356885	0.420362	0.430335
C	2.876336	-0.360067	-0.521910
C	-0.718799	1.174681	0.057988
C	-2.165144	0.746806	-0.000657
C	-1.966499	-0.784908	-0.253399
C	-0.534081	-1.127278	0.275518
H	-2.661376	0.946943	0.955074
H	-2.747081	1.225313	-0.792175
H	-2.752641	-1.398960	0.198254
H	-1.980260	-0.955818	-1.333813
H	-0.553003	-1.494746	1.308296
H	-0.028003	-1.874976	-0.341814
H	2.244560	1.487106	0.279074
H	2.242755	0.063329	1.448014
H	3.072826	0.022004	-1.516850
H	3.064254	-1.413515	-0.347794

E(UMP2) = -271.717797245
Detailed UMP2 results:
Sum of electronic and zero-point energies= -271.570993
Sum of electronic and thermal energies= -271.563070
Sum of electronic and thermal enthalpies= -271.562125
Sum of electronic and thermal free energies= -271.604307

The RMP2/6-311G(d,p) optimized structure of transition state **ac**‡

ATOM	X	Y	Z
C	0.027475	-0.157387	-0.001418
C	2.398598	-0.018615	-0.636341
C	2.361529	0.054433	0.709316
C	-0.401306	-1.349313	0.033543
C	-1.905375	-0.820013	-0.090134
C	-1.960743	0.734563	0.158558
C	-0.510439	1.212906	-0.152957
H	-2.231819	-1.069945	-1.103723
H	-2.534691	-1.357713	0.622468
H	-2.725014	1.245555	-0.435186
H	-2.163256	0.915471	1.217751
H	-0.393269	1.594583	-1.172431
H	-0.128004	1.946385	0.559190

```
             H                     2.374622    -0.976068   -1.143285
             H                     2.462075     0.876247   -1.248504
             H                     2.309021    -0.842390    1.315321
             H                     2.396970     1.009968    1.224009
---------------------------------------------------------------------

E(RMP2) =  -271.753857096
Detailed RMP2 results:
Sum of electronic and zero-point energies=           -271.608597
Sum of electronic and thermal energies=              -271.600342
Sum of electronic and thermal enthalpies=            -271.599399
Sum of electronic and thermal free energies=         -271.641325
```