

**Supplementary Information: Comparing coupled cluster and composite quantum chemical methods for computing activation energies and reaction enthalpies of radical propagation reactions**

Timothy B. Huber<sup>1</sup> and Ralph A. Wheeler<sup>\*1</sup>

*Department of Chemistry and Biochemistry, Northern Illinois University,  
1425 W Lincoln Hwy. DeKalb, Illinois 60115, USA*

(\*Electronic mail: [rwheeler5@niu.edu](mailto:rwheeler5@niu.edu))

(Dated: 21 September 2024)

## A. Statistical Error Analysis

Statistical error within the manuscript are defined as follows:

- Change in property of interest ( $\Delta_p$ ), where  $p$  is the property of interest (i.e. activation energy or reaction enthalpy).

$$\Delta_p = p_{\text{measured}} - p_{\text{reference}} \quad (\text{S1})$$

- Mean Deviation (MD)

$$MD = \frac{1}{N} \sum_i^N \Delta_{p_i} \quad (\text{S2})$$

- Mean Absolute Deviation (MAD)

$$MAD = \frac{1}{N} \sum_i^N |\Delta_{p_i}| \quad (\text{S3})$$

- Maximum Absolute Deviation (MaxAD)

$$MaxAD = \text{MAX}(|\Delta_{p_i}|) \quad (\text{S4})$$

- Corrected Sample Standard Deviation (SD)

$$SD = \sqrt{\frac{\sum_i^N |\Delta_{p_i} - MD|^2}{N - 1}} \quad (\text{S5})$$

## B. Multi-Reference Diagnostics

- $T_1$  diagnostic: obtained from canonical CCSD(T)/aug-cc-pVTZ calculations in Orca
- $\langle S^2 \rangle$  diagnostic: obtained from UHF calculations in Orca
- $\Delta \langle S^2 \rangle$  diagnostic: Relative deviation (%) from the exact  $\langle S^2 \rangle$  expectation value indicating spin-symmetry breaking:

$$\Delta \langle S^2 \rangle = \frac{|\langle S^2 \rangle_{method} - \langle S^2 \rangle_{exact}|}{\langle S^2 \rangle_{exact}} * 100 \quad (S6)$$

TABLE S1. Spin operator ( $\langle S^2 \rangle$ ), spin operator deviation error ( $\Delta \langle S^2 \rangle$ ), and T1 diagnostic values for the open-shell species amongst the 18 free radical polymerization systems. The properties were computed using UHF/cc-pVTZ, UHF-CCSD(T)/aug-cc-pVTZ, and UB3LYP-CCSD(T)/aug-cc-pVTZ.

System	Fragment	UHF		UHF-CCSD(T)			UB3LYP-CCSD(T)		
		$\langle S^2 \rangle$	$\Delta \langle S^2 \rangle$	$\langle S^2 \rangle$	$\Delta \langle S^2 \rangle$	T1 diagnostic	$\langle S^2 \rangle$	$\Delta \langle S^2 \rangle$	T1 diagnostic
	methyl	0.761661	1.6	0.761738	1.6	0.008618509	0.761738	1.6	0.008618509
	acetonitrile	0.935696	24.8	0.935091	24.7	0.035086599	0.935091	24.7	0.035086599
	methanol	0.761917	1.6	0.76227	1.6	0.015733226	0.76227	1.6	0.015733226
1	TS	1.000417	33.4	0.987294	31.6	0.031025885	0.987294	31.6	0.030603388
	product	0.763238	1.8	0.763344	1.8	0.010709568	0.763344	1.8	0.010709568
2	TS	0.997832	33.0	0.987294	31.6	0.031025885	0.987294	31.6	0.031025885
	product	0.764402	1.9	0.764521	1.9	0.011012768	0.764521	1.9	0.011012768
3	TS	0.996346	32.8	0.983012	31.1	0.024880423	0.983012	31.1	0.024880423
	product	0.764283	1.9	0.764389	1.9	0.01080938	0.764389	1.9	0.01080938
4	TS	0.995225	32.7	0.983012	31.1	0.024880423	0.983012	31.1	0.024880423
	product	0.764607	1.9	0.764687	2.0	0.011218815	0.764687	2.0	0.011218815
5	TS	0.960289	28.0	0.983012	31.1	0.024880423	0.983012	31.1	0.024880423
	product	0.76189	1.6	0.761949	1.6	0.013870978	0.761949	1.6	0.013870978
6	TS	0.986667	31.6	0.985364	31.4	0.024418507	0.985364	31.4	0.024418507
	product	0.76167	1.6	0.761821	1.6	0.013628154	0.761821	1.6	0.013628154
7	TS	0.975441	30.1	0.987294	31.6	0.031025885	0.987294	31.6	0.031025885
	product	0.76283	1.7	0.762938	1.7	0.01582162	0.762938	1.7	0.01582162
8	TS	0.995159	32.7	0.983012	31.1	0.024880423	0.983012	31.1	0.024880423
	product	0.767059	2.3	0.767448	2.3	0.012938077	0.767448	2.3	0.012938077
9	TS	0.985462	31.4	0.983012	31.1	0.024880423	0.983012	31.1	0.024880423
	product	0.762735	1.7	0.762911	1.7	0.012221537	0.762911	1.7	0.012221537
10	TS	0.993722	32.5	0.99289	32.4	0.026037854	0.99289	32.4	0.026037854
	product	0.766668	2.2	0.766926	2.3	0.012538226	0.766926	2.3	0.012538226
11	TS	1.006789	34.2	0.99289	32.4	0.026037854	0.99289	32.4	0.026037854
	product	0.768262	2.4	0.768664	2.5	0.01357162	0.768664	2.5	0.01357162
12	TS	0.993466	32.5	0.99289	32.4	0.026037854	0.99289	32.4	0.026037854
	product	0.794931	6.0	0.794068	5.9	0.016303846	0.756297	0.8	0.011340002
13	TS	0.99289	32.4	0.99289	32.4	0.026037854	0.99289	32.4	0.026037854
	product	0.926371	23.5	0.794068	5.9	0.016303846	0.926374	32.4	0.017208656
14	TS	1.120165	49.4	1.113515	48.5	0.035607735	0.99289	32.4	0.026037854
	product	0.9071	20.9	0.904488	20.6	0.02491674	0.765693	2.1	0.02491674
15	TS	1.117957	49.1	1.115758	48.8	0.032777432	0.77775	3.7	0.015034552
	product	0.919674	22.6	0.918905	22.5	0.024256591	0.764649	2.0	0.011323133
16	TS	0.986135	31.5	0.984007	31.2	0.029321177	0.984007	31.2	0.029321177
	product	0.763371	1.8	0.763486	1.8	0.011738446	0.763486	1.8	0.011738446
17	TS	1.115702	48.8	1.113349	48.4	0.034042284	1.113349	48.4	0.034042284
	product	0.76313	1.8	0.76326	1.8	0.012427795	0.76326	1.8	0.012427795
18	product	1.324506	76.6	1.32281	76.4	0.03252394	0.777311	3.6	0.010035777

## C. Scaled Zero-Point Energies

TABLE S2. Scaled ( $\times 0.9764$ ) zero point energies (Ha) for the substituted olefin, transition state (TS), and product radical of 18 radical addition reactions computed using B3LYP/cc-pVTZ.

System	Fragment	Zero-point energy
1	methyl	0.02896598
	methylcyanide	0.030246431
	methylhydroxy	0.036252756
2	olefin	0.049714382
	TS	0.082303197
	Product	0.085946243
3	olefin	0.077528503
	TS	0.109558817
	product	0.113404661
4	olefin	0.105526773
	TS	0.137511977
	product	0.141314763
5	olefin	0.104913887
	TS	0.13669932
	product	0.141246219
6	olefin	0.110067619
	TS	0.142014646
	product	0.146945271
7	olefin	0.110492548
	TS	0.141714208
	product	0.146919299
8	olefin	0.09177125
	TS	0.123764656
	product	0.128224851
9	olefin	0.041543184
	TS	0.073618021
	product	0.07832837
10	olefin	0.065137499
	TS	0.097252662
	product	0.101881286
11	olefin	0.068965671
	TS	0.100813886
	product	0.106117398
12	olefin	0.032731271
	TS	0.064544824
	product	0.070749163
13	olefin	0.092763663
	TS	0.124652301
	product	0.129807107
14	olefin	0.049497622
	TS	0.081410377
	product	0.086489414
15	olefin	0.059750212
	TS	0.091586613
	product	0.097366217
16	olefin	0.076876366
	TS	0.108555566
	product	0.113669949
17	olefin	0.088506364
	TS	0.091129658
	product	0.082931706
18	olefin	0.085316856
	TS	0.129957668
	product	0.161714981
		0.166797045

## D. Coupled Cluster Statistical Analysis and Statistical Analysis Summaries Using an Experimental Reference

TABLE S3. Statistical comparison (kJ/mol) of CCSD(T)/aug-cc-pVTZ and DLPNO-CCSD(T)/CBS with UHF reference orbitals to that with B3LYP orbitals for 18 radical addition reactions. Statistical properties for activation energies ( $E_A$ ) and reaction enthalpies ( $\Delta H_r$ ) include mean deviation (MD), mean absolute deviation (MAD), maximum absolute deviation (MaxAD), and standard deviation (SD).

Method	Property	MD	MAD	MaxAD	SD
UHF-CCSD(T)/aug-cc-pVTZ	$E_A$	3.0	3.0	6.3	1.9
	$\Delta H_r$	1.4	1.4	4.6	1.8
UHF-DLPNO-CCSD(T)/CBS	$E_A$	3.5	3.5	6.6	1.4
	$\Delta H_r$	1.4	1.5	4.4	1.5
UB3LYP-DLPNO-CCSD(T)/CBS	$E_A$	3.9	3.9	7.6	1.5
	$\Delta H_r$	1.1	1.4	4.6	1.6

TABLE S4. Statistical comparison (kJ/mol) of the activation energies using all computational methods in this study against experimental values for 17 radical addition reactions. Statistical properties for activation energies ( $E_A$ ) and reaction enthalpies ( $\Delta H_r$ ) include mean deviation (MD), mean absolute deviation (MAD), maximum absolute deviation (MaxAD), and standard deviation (SD).

	CBS-RAD	G3(MP2)-RAD	UHF-DLPNO/ CBS	UB3LYP-DLPNO/ CBS	UHF-CCSD(T)/ aug-cc-pVTZ	UB3LYP-CCSD(T)/ aug-cc-pVTZ
<b>Absolute values</b>						
MD	-2.2	5.1	4.4	4.8	3.9	0.9
MAD	2.2	5.5	4.9	5.3	4.6	2.9
MaxAD	9.3	10.0	11.6	11.5	10.6	8.9
SD	2.4	2.7	3.4	3.2	3.4	3.8
<b>Relative values<sup>a</sup></b>						
MD	-1.5	-0.6	-0.8	-1.3	-0.7	-1.5
MAD	1.5	1.8	2.2	2.2	2.1	2.7
MaxAD	8.6	8.6	9.7	10.5	10.8	11.2
SD	2.4	2.7	3.4	3.3	3.4	3.8

<sup>a</sup> Relative values were calculated as the difference between reaction enthalpy for the given reaction and the corresponding value for the unsubstituted olefin (system 1)

TABLE S5. Statistical comparison (kJ/mol) of the reaction enthalpies using all computational methods in this study against experimental values for 18 radical addition reactions. Statistical properties for activation energies ( $E_A$ ) and reaction enthalpies ( $\Delta H_r$ ) include mean deviation (MD), mean absolute deviation (MAD), maximum absolute deviation (MaxAD), and standard deviation (SD).

	CBS-RAD	G3(MP2)-RAD	UHF-DLPNO/ CBS	UB3LYP-DLPNO/ CBS	UHF-CCSD(T)/ aug-cc-pVTZ	UB3LYP-CCSD(T)/ aug-cc-pVTZ
<b>Absolute values</b>						
MD	-3.1	4.8	-2.6	-2.8	-1.9	-3.8
MAD	4.2	5.2	5.6	6.0	6.5	6.3
MaxAD	14.7	14.6	16.5	17.6	22.4	17.8
SD	4.9	4.3	7.1	7.5	8.9	7.5
<b>Relative values<sup>a</sup></b>						
MD	-5.1	-2.4	-3.8	-4.2	-3.1	-4.0
MAD	5.2	4.0	6.5	6.8	7.1	6.5
MaxAD	16.7	10.3	17.8	19.0	22.4	17.9
SD	4.9	4.5	7.7	7.8	9.2	7.6

<sup>a</sup> Relative values were calculated as the difference between reaction enthalpy for the given reaction and the corresponding value for the unsubstituted olefin (system 1)

## E. Electronic Energies

TABLE S6. Electronic energies [Hartree] computed with CCSD(T) and DLPNO-CCSD(T) for 18 radical addition reactions.

System	Fragment	UHF-CCSD(T)	UKS-CCSD(T)	norm UHF-DLPNO	norm UKS-DLPNO	tight UHF-DLPNO	tight UKS-DLPNO
1	methyl	-39.7636554	-39.76288541	-39.779104	-39.77818296	-39.77926315	-39.77818296
	methylcyanide	-131.8718253	-131.8699962	-131.9215371	-131.9187535	-131.9217984	-131.9190993
	methylhydroxy	-114.8988565	-114.8976338	-114.9459665	-114.9444241	-114.9461074	-114.9443716
	olefin	-78.44354722	-78.4416847	-78.475401	-78.47375566	-78.47550572	-78.47370168
2	TS	-118.1974515	-118.1956466	-118.2445377	-118.2416119	-118.2445585	-118.2415441
	Product	-118.2495911	-118.2473295	-118.2968194	-118.2942006	-118.2969754	-118.2942858
	olefin	-117.6901194	-117.6878137	-117.737843	-117.7353963	-117.738002	-117.7353977
	TS	-157.4441003	-157.4416325	-157.5071136	-157.503547	-157.5070794	-157.5032952
3	product	-157.496576	-157.4935993	-157.5599487	-157.5565645	-157.5600478	-157.556445
	olefin	-156.932363	-156.9292852	-156.9956579	-156.9924595	-156.9958579	-156.9923951
	TS	-196.6864647	-196.683235	-196.7649742	-196.7607099	-196.7649543	-196.7603129
	product	-196.738941	-196.7351716	-196.8178778	-196.8138028	-196.8180025	-196.8135498
4	olefin	-156.9380148	-156.9349432	-157.0013613	-156.9983026	-157.0017387	-156.9983234
	TS	-196.6925404	-196.6893336	-196.7711917	-196.7671017	-196.7711874	-196.7666335
	product	-196.7434386	-196.7397528	-196.8224864	-196.8184291	-196.8224992	-196.8180688
	olefin	-232.0613341	-232.0568677	-232.1550748	-232.1518957	-232.1557649	-232.1519293
5	TS	-271.814612	-271.8109637	-271.9231591	-271.9191486	-271.9233855	-271.9186814
	product	-271.8652335	-271.8610989	-271.9740658	-271.970185	-271.9743686	-271.9698012
	olefin	-232.0582161	-232.0547364	-232.1519057	-232.1486282	-232.1525766	-232.1486891
	TS	-271.80931	-271.8056998	-271.9180534	-271.9139243	-271.9182813	-271.9134673
6	product	-271.8655289	-271.8613237	-271.9745232	-271.9705178	-271.9748496	-271.9701052
	olefin	-306.0061021	-306.0021808	-306.1284428	-306.1253768	-306.1296522	-306.125476
	TS	-345.7610196	-345.7569367	-345.8981272	-345.8941538	-345.8985938	-345.8936499
	product	-345.8205072	-345.8158733	-345.9578348	-345.9542626	-345.9585818	-345.9538223
7	olefin	-537.5847223	-537.579643	-537.6493904	-537.6440036	-537.6498089	-537.6440812
	TS	-577.3408758	-577.3356947	-577.4207761	-577.4142213	-577.4208736	-577.4140555
	product	-577.396999	-577.3912637	-577.4771667	-577.4711903	-577.4774414	-577.4710141
	olefin	-368.7022574	-368.697566	-368.7505656	-368.7446073	-368.7507899	-368.7446478
8	TS	-408.4582931	-408.4534089	-408.5217324	-408.5146737	-408.5218268	-408.5145079
	product	-408.5127809	-408.5073792	-408.5766672	-408.5699902	-408.5768913	-408.5699062
	olefin	-576.8348829	-576.8290233	-576.9149929	-576.9089323	-576.9156076	-576.9090645
	TS	-616.5911561	-616.5852318	-616.6865125	-616.6794236	-616.6866088	-616.6790617
9	product	-616.6467264	-616.6402706	-616.7423232	-616.7354131	-616.742552	-616.7353093
	olefin	-996.7205892	-996.7119988	-996.817804	-996.8087801	-996.8186847	-996.8090824
	TS	-1036.478948	-1036.470372	-1036.591389	-1036.581367	-1036.591576	-1036.581026
	product	-1036.540392	-1036.531234	-1036.652811	-1036.643381	-1036.653259	-1036.643137
10	olefin	-306.0082741	-306.0027687	-306.1303882	-306.127471	-306.1316552	-306.127471
	TS	-345.767047	-345.7630438	-345.9043863	-345.9001305	-345.9048084	-345.8997277
	product	-345.8235744	-345.8190617	-345.9612299	-345.9573119	-345.961843	-345.9569625
	olefin	-170.543795	-170.5397917	-170.6082563	-170.6053158	-170.6087918	-170.6054172
11	TS	-210.301969	-210.2994815	-210.3826315	-210.3782832	-210.3826578	-210.3781127
	product	-210.3621785	-210.3589049	-210.4431743	-210.4389779	-210.4433831	-210.4389488
	olefin	-191.6074823	-191.6036862	-191.6833289	-191.6804848	-191.6840064	-191.6808025
	TS	-231.3671781	-231.3649702	-231.4592049	-231.455107	-231.4592127	-231.4549561
12	product	-231.4289896	-231.425915	-231.5211201	-231.5173278	-231.5213365	-231.5171653
	olefin	-209.7920607	-209.7871605	-209.8720236	-209.8684275	-209.8726392	-209.8685356
	TS	-249.5501544	-249.5468647	-249.6461968	-249.641408	-249.6461993	-249.6410272
	product	-249.611733	-249.6077458	-249.70768	-249.7028463	-249.7076956	-249.7024977
13	olefin	-78.44354722	-78.4416847	-78.475401	-78.47375566	-78.47550572	-78.47370168
	TS	-193.3331977	-193.3310978	-193.4115359	-193.4082847	-193.4116511	-193.4082643
	product	-193.3792513	-193.3764805	-193.4576355	-193.4546868	-193.4578632	-193.454677
	olefin	-78.44354722	-78.4416847	-78.475401	-78.47375566	-78.47550572	-78.47370168
14	TS	-210.305364	-210.3027076	-210.3860443	-210.3817216	-210.3862881	-210.381868
	product	-210.3484608	-210.3446454	-210.4285756	-210.42468	-210.4289059	-210.4246253
	olefin	-309.059828	-309.0530203	-309.1979862	-309.1922052	-309.1986704	-309.1923065
	product	-348.8750066	-348.8713948	-349.0360109	-349.0288592	-349.03609	-349.0282988