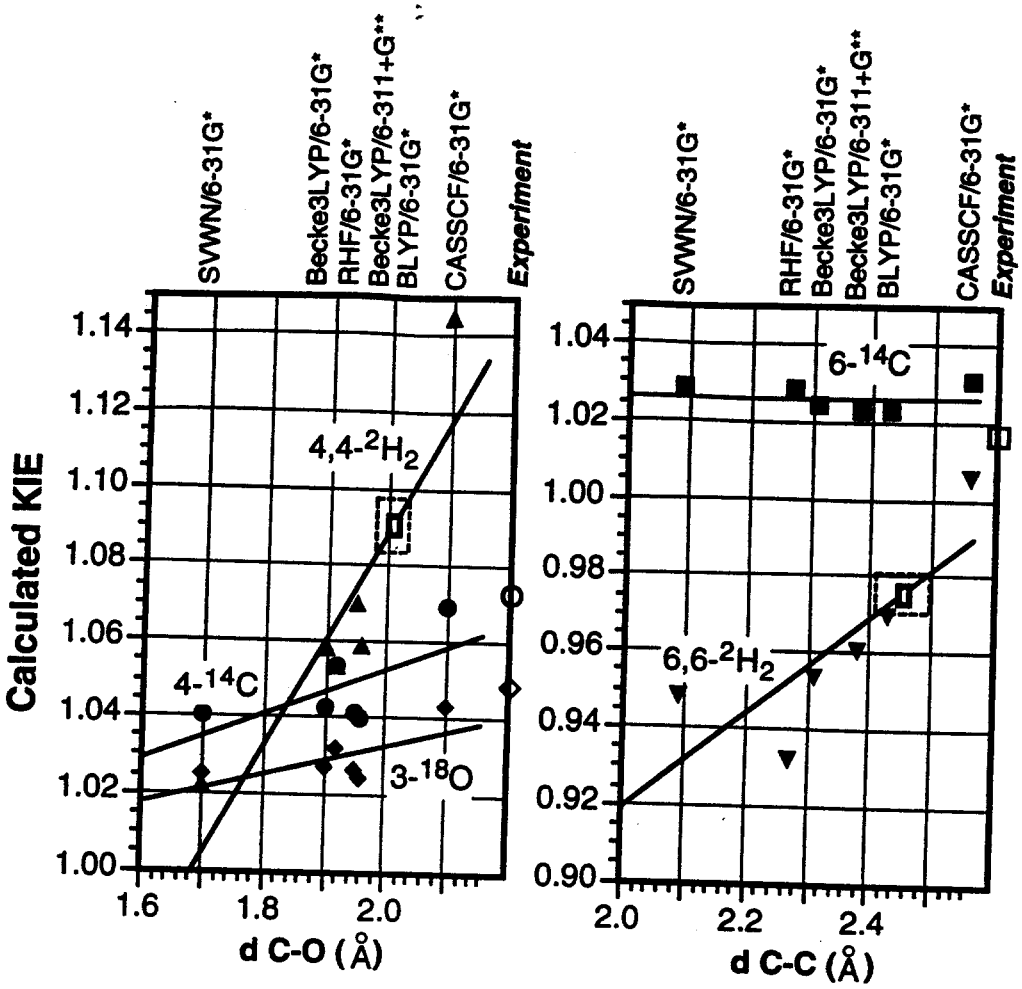

Figure: Calculated Kinetic Isotope Effects versus lengths of the breaking (left) and forming bond (right). Rectangular boxes represent the experimental error limits for the H/D SKIE. Experimental values of the heavy atom KIE are plotted on the right axis.

Cope Reactant: 1,5-Hexadiene Ci Symmetry

S-VWN/6-31G*:

E = -233.26437193 h ZPE = 0.13872680 h

1	6	.000000	.000000	-.763215
2	6	.000000	.000000	.763215
3	6	1.373308	.000000	-1.325141
4	6	-1.373308	.000000	1.325141
5	6	1.874952	-.943149	-2.120979
6	6	-1.874952	.943149	2.120979
7	1	-.555057	.896470	-1.106449
8	1	-.561912	-.877758	-1.138464
9	1	.561912	.877758	1.138464
10	1	.555057	-.896470	1.106449
11	1	2.012530	.846314	-1.026388
12	1	-2.012530	-.846314	1.026388
13	1	1.267955	-1.802491	-2.434597
14	1	2.902221	-.899420	-2.498129
15	1	-1.267955	1.802491	2.434597
16	1	-2.902221	.899420	2.498129

B-LYP/6-31G*:

E = -234.46714578 h ZPE = 0.13835830 h

1	6	.000000	.000000	-.781421
2	6	.000000	.000000	.781421
3	6	1.396176	.000000	-1.365052
4	6	-1.396176	.000000	1.365052
5	6	1.916143	-.963577	-2.144198
6	6	-1.916143	.963577	2.144198
7	1	-.550068	.897909	-1.123867
8	1	-.562860	-.876538	-1.150830
9	1	.562860	.876538	1.150830
10	1	.550068	-.897909	1.123867
11	1	2.020520	.866521	-1.103072
12	1	-2.020520	-.866521	1.103072
13	1	1.335985	-1.847074	-2.433747
14	1	2.938737	-.906323	-2.529303
15	1	-1.335985	1.847074	2.433747
16	1	-2.938737	.906323	2.529303

B-LYP/6-311+G**:

E = -234.54457219 h ZPE = 0.13724610 h

1	6	.000000	.000000	-.780526
2	6	.000000	.000000	.780526
3	6	1.392952	.000000	-1.367199
4	6	-1.392952	.000000	1.367199
5	6	1.899091	-.943309	-2.175331
6	6	-1.899091	.943309	2.175331
7	1	-.542622	.898380	-1.122786
8	1	-.563155	-.871471	-1.150950
9	1	.563155	.871471	1.150950
10	1	.542622	-.898380	1.122786
11	1	2.025391	.851497	-1.089320
12	1	-2.025391	-.851497	1.089320
13	1	1.311107	-1.811209	-2.483739
14	1	2.916928	-.880187	-2.562451
15	1	-1.311107	1.811209	2.483739
16	1	-2.916928	.880187	2.562451

Becke3-LYP/6-31G*:
E = -234.61174102 h ZPE = 0.14248930 h

1	6	.000000	.000000	-.774098
2	6	.000000	.000000	.774098
3	6	1.388908	.000000	-1.351933
4	6	-1.388908	.000000	1.351933
5	6	1.900750	-.952362	-2.132413
6	6	-1.900750	.952362	2.132413
7	1	-.545589	.890859	-1.117528
8	1	-.556854	-.871432	-1.142646
9	1	.556854	.871432	1.142646
10	1	.545589	-.890859	1.117528
11	1	2.012245	.856033	-1.085077
12	1	-2.012245	-.856033	1.085077
13	1	1.320109	-1.825128	-2.425940
14	1	2.917033	-.896673	-2.513739
15	1	-1.320109	1.825128	2.425940
16	1	-2.917033	.896673	2.513739

Becke3-LYP/6-311+G**
E = -234.68259512 h ZPE = 0.14120930 h

1	6	.000000	.000000	-.773102
2	6	.000000	.000000	.773102
3	6	1.385805	.000000	-1.353184
4	6	-1.385805	.000000	1.353184
5	6	1.885683	-.934459	-2.158936
6	6	-1.885683	.934459	2.158936
7	1	-.538945	.891873	-1.116585
8	1	-.557513	-.867162	-1.142884
9	1	.557513	.867162	1.142884
10	1	.538945	-.891873	1.116585
11	1	2.016981	.842727	-1.071972
12	1	-2.016981	-.842727	1.071972
13	1	1.297415	-1.793387	-2.469092
14	1	2.898428	-.873307	-2.541603
15	1	-1.297415	1.793387	2.469092
16	1	-2.898428	.873307	2.541603

Cope Chair Transition State: C2h symmetry
S-VWN/6-31G*:
E = -233.23321201 h ZPE = 0.13918600 h ν_{imag} = -188.656 cm^{-1}

1	6	.000000	1.421950	.000000
2	6	.000000	-1.421950	.000000
3	6	.386434	.786458	1.207620
4	6	-.386434	-.786458	1.207620
5	6	.386434	.786458	-1.207620
6	6	-.386434	-.786458	-1.207620
7	1	-.939365	1.993054	.000000
8	1	.939365	-1.993054	.000000
9	1	.051311	1.260918	2.143337
10	1	-.051311	-1.260918	2.143337
11	1	.051311	1.260918	-2.143337
12	1	-.051311	-1.260918	-2.143337
13	1	1.450116	.510753	1.279967
14	1	-1.450116	-.510753	1.279967
15	1	1.450116	.510753	-1.279967
16	1	-1.450116	-.510753	-1.279967

B-LYP/6-31G*:

E = -234.41908449 h ZPE = 0.13764540 h ν_{imag} = -505.285 cm^{-1}

1	6	.000000	1.472428	.000000
2	6	.000000	-1.472428	.000000
3	6	.431559	.920910	1.228532
4	6	-.431559	-.920910	1.228532
5	6	.431559	.920910	-1.228532
6	6	-.431559	-.920910	-1.228532
7	1	-.942103	2.037182	.000000
8	1	.942103	-2.037182	.000000
9	1	.049232	1.352056	2.161688
10	1	-.049232	-1.352056	2.161688
11	1	.049232	1.352056	-2.161688
12	1	-.049232	-1.352056	-2.161688
13	1	1.469615	.581042	1.310549
14	1	-1.469615	-.581042	1.310549
15	1	1.469615	.581042	-1.310549
16	1	-1.469615	-.581042	-1.310549

B-LYP/6-311+G**:

E = -234.49548828 h ZPE = 0.13595240 h ν_{imag} = -469.938 cm^{-1}

1	6	.000000	1.482216	.000000
2	6	.000000	-1.482216	.000000
3	6	.452094	.972313	1.228610
4	6	-.452094	-.972313	1.228610
5	6	.452094	.972313	-1.228610
6	6	-.452094	-.972313	-1.228610
7	1	-.938021	2.046971	.000000
8	1	.938021	-2.046971	.000000
9	1	.050608	1.381065	2.158089
10	1	-.050608	-1.381065	2.158089
11	1	.050608	1.381065	-2.158089
12	1	-.050608	-1.381065	-2.158089
13	1	1.474026	.600403	1.309719
14	1	-1.474026	-.600403	1.309719
15	1	1.474026	.600403	-1.309719
16	1	-1.474026	-.600403	-1.309719

Becke3-LYP/6-31G*:

E = -234.55678802 h ZPE = 0.14198770 h ν_{imag} = -578.972 cm^{-1}

1	6	.000000	1.452827	.000000
2	6	.000000	-1.452827	.000000
3	6	.422252	.890387	1.218584
4	6	-.422252	-.890387	1.218584
5	6	.422252	.890387	-1.218584
6	6	-.422252	-.890387	-1.218584
7	1	-.931630	2.019785	.000000
8	1	.931630	-2.019785	.000000
9	1	.048274	1.325445	2.145338
10	1	-.048274	-1.325445	2.145338
11	1	.048274	1.325445	-2.145338
12	1	-.048274	-1.325445	-2.145338
13	1	1.457220	.563010	1.299818
14	1	-1.457220	-.563010	1.299818
15	1	1.457220	.563010	-1.299818
16	1	-1.457220	-.563010	-1.299818

Becke3-LYP/6-311+G**:

E = -234.62616996 h ZPE = 0.14026930 h ν_{imag} = -573.671 cm^{-1}

1	6	.000000	1.454868	.000000
2	6	.000000	-1.454868	.000000
3	6	.438001	.923072	1.218140
4	6	-.438001	-.923072	1.218140
5	6	.438001	.923072	-1.218140
6	6	-.438001	-.923072	-1.218140
7	1	-.928365	2.022273	.000000
8	1	.928365	-2.022273	.000000
9	1	.050749	1.342917	2.142126
10	1	-.050749	-1.342917	2.142126
11	1	.050749	1.342917	-2.142126
12	1	-.050749	-1.342917	-2.142126
13	1	1.461330	.572065	1.297546
14	1	-1.461330	-.572065	1.297546
15	1	1.461330	.572065	-1.297546
16	1	-1.461330	-.572065	-1.297546

Cope Boat Transition State: C2v

S-VWN/6-31G*:

E = -233.21061301 h ZPE = 0.13788100 h ν_{imag} = -508.579 cm^{-1}

1	6	.000000	1.392243	-.406564
2	6	.000000	-1.392243	-.406564
3	6	-1.205141	.982846	.172136
4	6	-1.205141	-.982846	.172136
5	6	1.205141	.982846	.172136
6	6	1.205141	-.982846	.172136
7	1	.000000	1.573410	-1.492141
8	1	.000000	-1.573410	-1.492141
9	1	-2.143803	1.246494	-.332520
10	1	-2.143803	-1.246494	-.332520
11	1	2.143803	1.246494	-.332520
12	1	2.143803	-1.246494	-.332520
13	1	-1.275597	1.065806	1.265467
14	1	-1.275597	-1.065806	1.265467
15	1	1.275597	1.065806	1.265467
16	1	1.275597	-1.065806	1.265467

B-LYP/6-31G*:

E = -234.40775326 h ZPE = 0.13638590 h ν_{imag} = -421.615 cm^{-1}

1	6	.000000	1.451351	-.415539
2	6	.000000	-1.451351	-.415539
3	6	-1.230831	1.144673	.178945
4	6	-1.230831	-1.144673	.178945
5	6	1.230831	1.144673	.178945
6	6	1.230831	-1.144673	.178945
7	1	.000000	1.641490	-1.497995
8	1	.000000	-1.641490	-1.497995
9	1	-2.163945	1.364115	-.347790
10	1	-2.163945	-1.364115	-.347790
11	1	2.163945	1.364115	-.347790
12	1	2.163945	-1.364115	-.347790
13	1	-1.311748	1.133969	1.269732
14	1	-1.311748	-1.133969	1.269732
15	1	1.311748	1.133969	1.269732
16	1	1.311748	-1.133969	1.269732

B-LYP/6-311+G**:

E = -234.48653602 h ZPE = 0.13495900 h ν_{imag} = -369.446 cm^{-1}

1	6	.000000	1.461533	-.417962
2	6	.000000	-1.461533	-.417962
3	6	-1.230933	1.188244	.181114
4	6	-1.230933	-1.188244	.181114
5	6	1.230933	1.188244	.181114
6	6	1.230933	-1.188244	.181114
7	1	.000000	1.655697	-1.495983
8	1	.000000	-1.655697	-1.495983
9	1	-2.159638	1.389742	-.352149
10	1	-2.159638	-1.389742	-.352149
11	1	2.159638	1.389742	-.352149
12	1	2.159638	-1.389742	-.352149
13	1	-1.310814	1.147428	1.267343
14	1	-1.310814	-1.147428	1.267343
15	1	1.310814	1.147428	1.267343
16	1	1.310814	-1.147428	1.267343

Becke3-LYP/6-31G*:

E = -234.54307794 h ZPE = 0.14074640 h ν_{imag} = -527.028 cm^{-1}

1	6	0.000000	1.429369	-0.412153
2	6	0.000000	-1.429369	-0.412153
3	6	-1.219742	1.104045	0.177018
4	6	-1.219742	-1.104045	0.177018
5	6	1.219742	1.104045	0.177018
6	6	1.219742	-1.104045	0.177018
7	1	0.000000	1.616661	-1.487212
8	1	0.000000	-1.616661	-1.487212
9	1	-2.147259	1.329162	-0.343097
10	1	-2.147259	-1.329162	-0.343097
11	1	2.147259	1.329162	-0.343097
12	1	2.147259	-1.329162	-0.343097
13	1	-1.298612	1.112781	1.261056
14	1	-1.298612	-1.112781	1.261056
15	1	1.298612	1.112781	1.261056
16	1	1.298612	-1.112781	1.261056

Becke3-LYP/6-311+G**:

E = -234.61471830 h ZPE = 0.13905840 h ν_{imag} = -479.348 cm^{-1}

1	6	0.000000	1.435589	-0.414597
2	6	0.000000	-1.435589	-0.414597
3	6	-1.219673	1.139426	0.178854
4	6	-1.219673	-1.139426	0.178854
5	6	1.219673	1.139426	0.178854
6	6	1.219673	-1.139426	0.178854
7	1	0.000000	1.629591	-1.485715
8	1	0.000000	-1.629591	-1.485715
9	1	-2.143985	1.350420	-0.346203
10	1	-2.143985	-1.350420	-0.346203
11	1	2.143985	1.350420	-0.346203
12	1	2.143985	-1.350420	-0.346203
13	1	-1.296094	1.119392	1.259725
14	1	-1.296094	-1.119392	1.259725
15	1	1.296094	1.119392	1.259725
16	1	1.296094	-1.119392	1.259725

Claisen Reactant: Allyl Vinyl Ether

S-VWN/6-31G*:

E = -269.02442543 h ZPE = 0.11630640 h

1	6	-1.346617	1.327084	.130911
2	6	-1.694114	.078619	-.193943
3	8	-.944186	-1.037387	-.106024
4	1	-2.084811	2.124571	.021771
5	1	-.342443	1.598953	.464423
6	1	-2.690222	-.174595	-.577401
7	6	.331831	-.882462	.473133
8	1	.247598	-.330939	1.434970
9	1	.660062	-1.914952	.697562
10	6	1.316795	-.221045	-.424404
11	6	2.255930	.622050	-.000388
12	1	1.258680	-.515171	-1.482179
13	1	2.313626	.924877	1.053823
14	1	3.008043	1.040878	-.676628

B-LYP/6-31G*:

E = -270.38410841 h ZPE = 0.11526900 h

1	6	-1.530886	1.306619	.124288
2	6	-1.737327	.022124	-.224015
3	8	-.899358	-1.063257	-.109810
4	1	-2.338019	2.025753	-.025501
5	1	-.593794	1.682758	.533699
6	1	-2.683257	-.314399	-.660509
7	6	.394029	-.863290	.518366
8	1	.279730	-.289215	1.456880
9	1	.708283	-1.889420	.778452
10	6	1.413178	-.226164	-.402125
11	6	2.299785	.709476	-.025515
12	1	1.422188	-.619636	-1.426297
13	1	2.312541	1.119227	.990827
14	1	3.054518	1.098404	-.715056

Becke3-LYP/6-31G*:

E = -270.50568350 h ZPE = 0.11901070 h

1	6	-1.503862	1.298556	.124490
2	6	-1.723613	.025782	-.216449
3	8	-.895718	-1.049478	-.108752
4	1	-2.299856	2.020765	-.017278
5	1	-.563727	1.662194	.519783
6	1	-2.671250	-.298246	-.639513
7	6	.382118	-.862164	.506130
8	1	.275354	-.300198	1.444129
9	1	.702424	-1.880775	.755132
10	6	1.392036	-.217777	-.405860
11	6	2.285581	.691497	-.018256
12	1	1.385747	-.583429	-1.432378
13	1	2.311121	1.073353	1.000993
14	1	3.032368	1.086810	-.701185

Becke3-LYP/ 6-311+G**:

E = -270.58837363 h ZPE = 0.11718990 h

1	6	-1.530886	1.306619	.124288
2	6	-1.737327	.022124	-.224015
3	8	-.899358	-1.063257	-.109810
4	1	-2.338019	2.025753	-.025501
5	1	-.593794	1.682758	.533699
6	1	-2.683257	-.314399	-.660509
7	6	.394029	-.863290	.518366
8	1	.279730	-.289215	1.456880
9	1	.708283	-1.889420	.778452
10	6	1.413178	-.226164	-.402125
11	6	2.299785	.709476	-.025515
12	1	1.422188	-.619636	-1.426297
13	1	2.312541	1.119227	.990827
14	1	3.054518	1.098404	-.715056

Claisen Transition States

S-VWN/6-31G*:

E = -268.98949689 h ZPE = 0.11459700 h ν_{imag} = -468.254 cm^{-1}

1	8	-.008391	-1.376856	-.280003
2	6	-1.051446	-.810904	.239437
3	6	-1.539890	.367374	-.286603
4	6	.125324	1.485668	.314763
5	6	1.159905	.776490	-.269781
6	6	1.387603	-.537578	.193543
7	1	-1.378703	.576708	-1.348588
8	1	-2.416165	.843267	.173401
9	1	-.185424	2.458664	-.086641
10	1	-.058963	1.369499	1.390415
11	1	1.446942	1.013731	-1.302248
12	1	2.158730	-1.144823	-.294442
13	1	1.348862	-.698784	1.281344
14	1	-1.337138	-1.089704	1.278624

B-LYP/6-31G*:

E = -270.34839257 h ZPE = 0.11321950 h ν_{imag} = -376.872 cm^{-1}

1	8	-.594675	-1.346506	-.256079
2	6	-1.335195	-.417930	.273747
3	6	-1.488855	.846168	-.286642
4	6	.791418	1.419390	.319175
5	6	1.410048	.349033	-.314797
6	6	1.274372	-.962498	.186283
7	1	-1.227114	1.016782	-1.331899
8	1	-2.136755	1.586922	.193735
9	1	.794490	2.419989	-.121630
10	1	.551393	1.376529	1.384116
11	1	1.728739	.469440	-1.356627
12	1	1.709036	-1.806585	-.352653
13	1	1.149403	-1.120152	1.260519
14	1	-1.722521	-.575858	1.306471

Becke3-LYP/6-31G*:

E = -270.46115395 h ZPE = 0.11714310 h ν_{imag} = -482.055 cm^{-1}

1	8	-.510949	-1.358154	-.250188
2	6	-1.292571	-.470771	.260912
3	6	-1.464704	.785492	-.290788
4	6	.670934	1.424244	.324093
5	6	1.373516	.411908	-.303075
6	6	1.284090	-.901152	.181006
7	1	-1.219981	.954782	-1.332912
8	1	-2.145663	1.494108	.175495
9	1	.631147	2.424874	-.097620
10	1	.447716	1.363662	1.384822
11	1	1.689276	.556288	-1.334569
12	1	1.763734	-1.713403	-.354566
13	1	1.175379	-1.068930	1.248379
14	1	-1.681595	-.644479	1.279582

Becke3-LYP/6-311+G**:

E = -270.54613326 h ZPE = 0.11582930 h ν_{imag} = -439.195 cm^{-1}

1	8	-.573954	-1.343908	-.242364
2	6	-1.316049	-.429773	.268881
3	6	-1.476164	.819593	-.293195
4	6	.749227	1.408342	.328564
5	6	1.387971	.370665	-.314847
6	6	1.290369	-.933595	.176517
7	1	-1.213490	.988068	-1.328762
8	1	-2.127671	1.546062	.181238
9	1	.723401	2.403433	-.099923
10	1	.518756	1.347754	1.384864
11	1	1.699466	.506969	-1.346004
12	1	1.721939	-1.759736	-.372464
13	1	1.165225	-1.102183	1.238906
14	1	-1.708115	-.590495	1.285544