

Understanding (the Lack of) Homolytic Substitution Chemistry of Sulfones

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Electronic Supplementary Information

Details of computational methods, Figures S1 and S2, Gaussian Archive entries
for **1** and **3** (13 pages).

Computational Details

Standard ab initio molecular orbital and DFT calculations were performed in Gaussian 09.^{S1} All geometry optimisations, frequency and single point energy calculations on open-shell species were performed using unrestricted wavefunctions. (U)RCCSD(T) calculations were performed using MOLPRO, version 2009.1.^{S2}

Geometries of all species in Scheme 4 were optimised at the B3LYP/6-31G(d), BHandHLYP/6-311G(d,p), and BHandHLYP/6-311++G(d,p) levels of theory. The BHandHLYP functional has been shown previously by us to perform well when modelling homolytic substitution chemistry, and triple- ζ basis sets provide superior results for single-point calculations. B3LYP/6-31G(d) is the standard optimization method for G3(MP2)-RAD calculations.^{S3} Frequency calculations were also performed at these levels, while geometries of all species in Scheme 6 were optimised at the B3LYP/6-31G(d) level. All transition states were shown to be “correct” through animation of the single imaginary frequency in GaussView. All ZPE corrections are unscaled.

Improved energies were calculated using QCISD and CCSD(T) methods. Further improved energies were then obtained using G3(MP2)-RAD, a high-level composite method that approximates (U)RCCSD(T) calculations with a large triple- ζ basis set via additivity corrections at the R(O)MP2 level of theory.^{S3} This approach has been shown to reproduce a large test set of gas-phase experimental data to within chemical accuracy,^{S3} and we have had success with the use of this method to model the kinetics and thermodynamics of radical cyclization reactions.^{S4,S5}

Gas-phase rate coefficients were calculated using standard transition state theory as has previously been described by us.^{S5}

References

- S1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Peterson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H.P.; Izmayl, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A. Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, K.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S.S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R.E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *GAUSSIAN 09 (Revision B.01)*, Gaussian, Inc., Wallingford, CT, **2010**.
- S2. Werner, H.-J.; Knowles, P. J.; Lindh, R.; Manby, F. R.; Schu'tz, M.; Celani, P.; Korona, T.; Rauhut, G.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C.; Hetzer, G.; Lloyd, A. W.; McNicholas, S. J.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pitzer, R.; Schumann, U.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteins- son, T. MOLPRO, version 2009.1, a package of ab initio programs.
- S3. D. J. Henry, M. B. Sullivan and L. Radom, *J. Chem. Phys.*, 2003, **118**, 4849.
- S4. S. Lobachevsky, C. H. Schiesser, C. Y. Lin and M. L. Coote, *J. Phys. Chem. A*, 2009, **112**, 13622.
- S5. S. H. Kyne, C. Y. Lin, I. Ryu, M. L. Coote and C. H. Schiesser, *Chem. Commun.*, 2010, **46**, 6521.

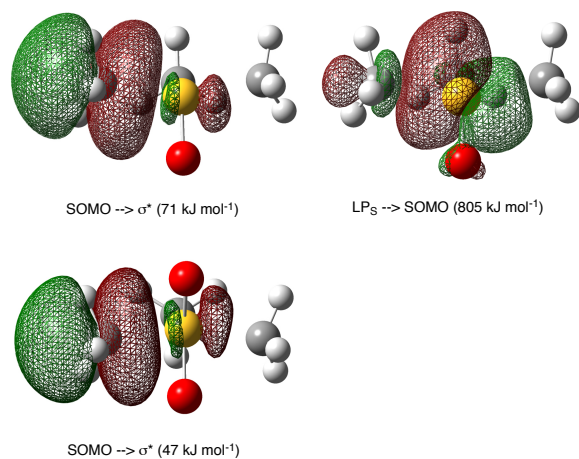


Figure S1 GaussView representations of key BHandHLYP/6-311G(d,p) generated orbitals for transition states **1** ($n = 1$, above) and **2** ($n = 2$, below).

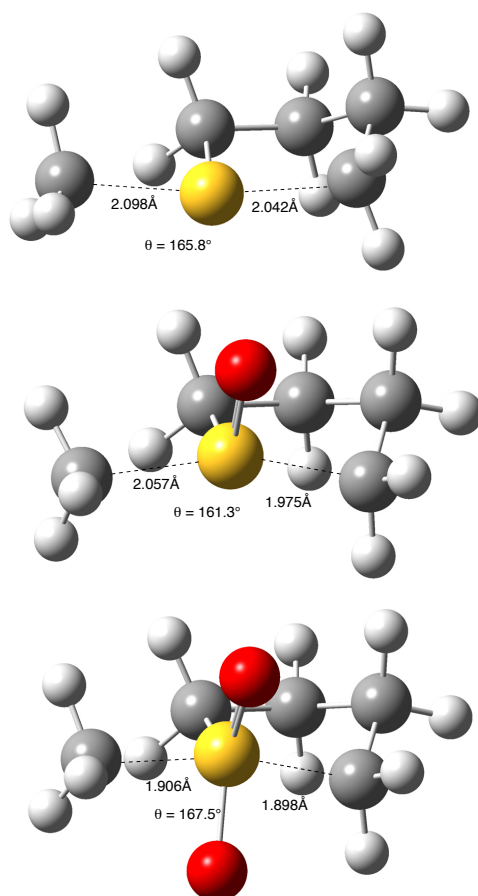


Figure S2 BHandHLYP/6-311G(d,p) Optimised structures of transition states **1** ($n = 1$, 2).

Gaussian Archive Entries

Transition state 1 (n = 0)

B3LYP/6-31G(d)

```
1\1\GINC-V1459\FTS\UB3LYP\Gen\C3H9S1(2)\HMA563\04-Apr-2012\0\#\B3LYP/g
en 6D INT(grid=ultrafine) OPT=(TS,calcfc,noeigentest,maxcyc=200) IOP(2
/17=4) Freq=noraman maxdisk=268435456\s-t.freq\0,2\S,-0.0128056207,0
.0859005579,0.0026279659\C,0.0552677479,-0.0858090482,2.0550514742\H,1
.0978175879,-0.0736151353,2.3764244153\H,-0.5171646924,0.7489001571,2.
4667571609\H,-0.419511531,-1.043629031,2.2673204858\C,0.4678497368,-0.
3217462362,-1.9593881151\H,0.0356038967,-1.3038162185,-2.1506892972\H,
1.5539639095,-0.3332841297,-2.0621507335\H,-0.0002929306,0.4521502475,
-2.5724441475\C,0.9396844282,1.65003686,0.0085899335\H,2.0112839538,1.
4614212232,0.1298083463\H,0.7711869921,2.1744136995,-0.9345312024\H,0.
58968425,2.2782763118,0.8305448574\\Version=EM64L-G09RevA.02\State=2-A
\HF=-517.8312007\S2=0.760708\S2-1=0.\S2A=0.750052\RMSD=7.586e-09\RMSF=
9.415e-06\Dipole=0.3484904,0.3195987,0.0173071\Quadrupole=-1.0484681,0
.6217892,0.4266789,0.6462551,-0.1934335,0.0540233\PG=C01 [X(C3H9S1)]\
@
```

BHandHLYP/6-311G(d,p)

```
1\1\GINC-GOMBERG02\FTS\UBHandHLYP\6-311++G(d,p)\C3H9S1(2)\HMAITKEN\07-
May-2012\0\#\BHandHLYP/6-311++G** OPT=(grad,readfc,ts,noeigentest) geo
m=checkpoint guess=read Freq=noraman\s-t.freq\0,2\S,0.346558348,0.39
57011873,0.0021956148\C,2.099439443,-0.6216023462,0.2286313506\H,2.522
4812858,-0.7952199486,-0.7510929296\H,2.7343683654,-0.0096506139,0.856
66869\H,1.8215726332,-1.5440488252,0.7160220878\C,-1.5223323091,0.8589
222525,-0.6713411809\H,-2.1565360889,0.0781063756,-0.2789644329\H,-1.5
076827059,0.859861146,-1.7522915029\H,-1.7692120889,1.8270531142,-0.25
50484125\C,1.1290401344,1.7454524314,-0.9174331633\H,1.2871480094,1.47
00748122,-1.9545936201\H,0.4940986283,2.6201869762,-0.8715451404\H,2.0
810891212,1.9787027202,-0.4596887174\\Version=AM64L-G09RevC.01\State=2
-A\HF=-517.7773799\S2=0.7744\S2-1=0.\S2A=0.750217\RMSD=3.110e-09\RMSF=
6.721e-05\Dipole=0.1920674,0.2695601,-0.3274166\Quadrupole=0.0902662,0
.6414854,-0.7317516,0.4713653,-0.1081754,-0.6423991\PG=C01 [X(C3H9S1)]
\\@
```

BHandHLYP/6-311++G(d,p)

```
1\1\GINC-GOMBERG02\FTS\UBHandHLYP\6-311++G(d,p)\C3H9S1(2)\HMAITKEN\07-
May-2012\0\#\BHandHLYP/6-311++G** OPT=(grad,readfc,ts,noeigentest) geo
m=checkpoint guess=read Freq=noraman\s-t.freq\0,2\S,0.346558348,0.39
57011873,0.0021956148\C,2.099439443,-0.6216023462,0.2286313506\H,2.522
4812858,-0.7952199486,-0.7510929296\H,2.7343683654,-0.0096506139,0.856
66869\H,1.8215726332,-1.5440488252,0.7160220878\C,-1.5223323091,0.8589
222525,-0.6713411809\H,-2.1565360889,0.0781063756,-0.2789644329\H,-1.5
076827059,0.859861146,-1.7522915029\H,-1.7692120889,1.8270531142,-0.25
50484125\C,1.1290401344,1.7454524314,-0.9174331633\H,1.2871480094,1.47
00748122,-1.9545936201\H,0.4940986283,2.6201869762,-0.8715451404\H,2.0
810891212,1.9787027202,-0.4596887174\\Version=AM64L-G09RevC.01\State=2
-A\HF=-517.7773799\S2=0.7744\S2-1=0.\S2A=0.750217\RMSD=3.110e-09\RMSF=
6.721e-05\Dipole=0.1920674,0.2695601,-0.3274166\Quadrupole=0.0902662,0
.6414854,-0.7317516,0.4713653,-0.1081754,-0.6423991\PG=C01 [X(C3H9S1)]
\\@
```

ROMP2/6-311G(d,p)//BHandHLYP/6-311G(d,p)

```
1\1\GINC-GOMBERG09\SP\ROMP2-FC\6-311G(d,p)\C3H9S1(2)\HMAITKEN\04-May-2012\0\0\#ROMP2/6-311G** geom=checkpoint guess=read\\s-t.freq\\0,2\S,0,0.032480107,0.0722720707,0.0082800381\C,0,0.0522347981,-0.0791933072,2.0439550877\H,0,1.0789085284,-0.0438246263,2.3798771732\H,0,-0.5408109325,0.7428085046,2.4225786571\H,0,-0.4049738725,-1.0347081209,2.2521485418\C,0,0.4596886144,-0.3119975553,-1.9505784082\H,0,0.0423724773,-1.2903207744,-2.1353037554\H,0,1.5333220635,-0.3036764895,-2.0746735916\H,0,-0.0351334431,0.4541437458,-2.5327448155\C,0,0.9551010235,1.630948288,0.0115516685\H,0,2.0182948078,1.4550191494,0.1309631015\H,0,0.7802238953,2.1475809976,-0.9225992679\H,0,0.6009131642,2.2501340261,0.8247102705\\Version=AM64L-G09RevC.01\State=2-A\HF=-516.284146\MP2=-516.911349\RMSD=6.549e-09\PG=C01 [X(C3H9S1)]\\@
```

QCISD/6-311G(d,p)//BHandHLYP/6-311G(d,p)

```
1\1\GINC-GOMBERG09\SP\UQCISD-FC\6-311G(d,p)\C3H9S1(2)\HMAITKEN\04-May-2012\0\0\#QCISD/6-311G** geom=checkpoint guess=read\\s-t.freq\\0,2\S,0,0.032480107,0.0722720707,0.0082800381\C,0,0.0522347981,-0.0791933072,2.0439550877\H,0,1.0789085284,-0.0438246263,2.3798771732\H,0,-0.5408109325,0.7428085046,2.4225786571\H,0,-0.4049738725,-1.0347081209,2.2521485418\C,0,0.4596886144,-0.3119975553,-1.9505784082\H,0,0.0423724773,-1.2903207744,-2.1353037554\H,0,1.5333220635,-0.3036764895,-2.0746735916\H,0,-0.0351334431,0.4541437458,-2.5327448155\C,0,0.9551010235,1.630948288,0.0115516685\H,0,2.0182948078,1.4550191494,0.1309631015\H,0,0.7802238953,2.1475809976,-0.9225992679\H,0,0.6009131642,2.2501340261,0.8247102705\\Version=AM64L-G09RevC.01\State=2-A\HF=-516.2990728\MP2=-516.9028951\MP3=-516.9572364\MP4D=-516.9735821\MP4DQ=-516.9608846\PUHF=-516.310153\PMP2-0=-516.911076\PMP3-0=-516.9622965\MP4SDQ=-516.966633\QCISD=-516.9700968\S2=0.831022\S2-1=0.78793\S2A=0.752219\RMSD=2.759e-09\PG=C01 [X(C3H9S1)]\\@
```

CCSD(T)/6-311G(d,p)//BHandHLYP/6-311G(d,p)

```
1\1\GINC-GOMBERG09\SP\UCCSD(T)-FC\6-311G(d,p)\C3H9S1(2)\HMAITKEN\04-May-2012\0\0\#CCSD(T)/6-311G** geom=checkpoint guess=read\\s-t.freq\\0,2\S,0,0.032480107,0.0722720707,0.0082800381\C,0,0.0522347981,-0.0791933072,2.0439550877\H,0,1.0789085284,-0.0438246263,2.3798771732\H,0,-0.5408109325,0.7428085046,2.4225786571\H,0,-0.4049738725,-1.0347081209,2.2521485418\C,0,0.4596886144,-0.3119975553,-1.9505784082\H,0,0.0423724773,-1.2903207744,-2.1353037554\H,0,1.5333220635,-0.3036764895,-2.0746735916\H,0,-0.0351334431,0.4541437458,-2.5327448155\C,0,0.9551010235,1.630948288,0.0115516685\H,0,2.0182948078,1.4550191494,0.1309631015\H,0,0.7802238953,2.1475809976,-0.9225992679\H,0,0.6009131642,2.2501340261,0.8247102705\\Version=AM64L-G09RevC.01\State=2-A\HF=-516.2990728\MP2=-516.9028951\MP3=-516.9572364\MP4D=-516.9735821\MP4DQ=-516.9608846\PUHF=-516.310153\PMP2-0=-516.911076\PMP3-0=-516.9622965\MP4SDQ=-516.966633\CCSD=-516.9688978\CCSD(T)=-516.9917751\S2=0.831022\S2-1=0.78793\S2A=0.752219\RMSD=2.759e-09\PG=C01 [X(C3H9S1)]\\@
```

Transition state 1 (n = 1)

B3LYP/6-31G(d)

```
1\1\GINC-V1353\FTS\UB3LYP\Gen\C3H9O1S1(2)\HMA563\04-Apr-2012\0\0\#B3LYP/gen 6D INT(grid=ultrafine) OPT=(TS,calcfc,noeigentest,maxcyc=200) IOP
```

```
(2/17=4) Freq=noraman maxdisk=268435456\\s_o-t.freq\\0,2\\S,-0.00287496
95,-0.1089629498,0.0462319856\\O,-0.0352712517,-0.1545620272,1.55192372
18\\C,2.0038750935,0.0610932889,-0.2466803719\\H,2.2458334157,1.04652351
52,0.1520385688\\H,2.4799004808,-0.7326169191,0.3325031525\\H,2.21552077
41,-0.0094030832,-1.3161724594\\C,-1.9726580756,0.2403975874,-0.3267735
485\\H,-2.1410130412,1.2437825505,0.0649796163\\H,-2.5410522394,-0.50710
86966,0.230196018\\H,-2.1463166463,0.1887574464,-1.4041565733\\C,-0.0650
601569,-1.8031937197,-0.6639602726\\H,-0.9878960911,-2.2882938831,-0.34
13212278\\H,-0.0398348448,-1.7295618587,-1.7560586107\\H,0.7965910688,-2
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007675\\S2=0.760421\\S2-1=0.\\S2A=0.750056\\RMSD=5.795e-09\\RMSF=4.100e-06\\
Dipole=0.0127932,-0.3583013,-1.3338335\\Quadrupole=1.3503374,1.9364846,
-3.286822,0.0255809,0.1012937,0.0846592\\PG=C01 [X(C3H9O1S1)]\\@
```

BHandHLYP/6-311G(d,p)

```
1\\1\\GINC-GOMBERG19\\FTS\\UBHandHLYP\\6-311G(d,p)\\C3H9O1S1(2)\\HMAITKEN\\17-
Apr-2012\\0\\#BHandHLYP/6-311G** 6D INT(grid=ultrafine) OPT=(TS,calcfc,
noeigentest,maxcyc=200) IOP(2/17=4) Freq=noraman\\s_o-t.bh.freq\\0,2\\S
,-0.0025281336,-0.1191402595,0.02726806\\O,-0.0349705914,-0.200938468,1
.5119970271\\C,1.9702961625,0.0570803563,-0.2416938493\\H,2.2029497524,1
.0434901834,0.1319463471\\H,2.4348294229,-0.7130585514,0.3593689441\\H,2
.1899466703,-0.0365013069,-1.2975473186\\C,-1.9393127861,0.2352074728,-
0.3173082184\\H,-2.0955820867,1.2393371573,0.0488099573\\H,-2.4947742087
,-0.4884590859,0.2640272171\\H,-2.1256542913,0.1601233595,-1.3810138363
\\C,-0.0648156521,-1.7835127958,-0.6729962097\\H,-0.978914936,-2.2600883
117,-0.3473704318\\H,-0.0407675277,-1.7150393641,-1.7550893125\\H,0.7889
301029,-2.340633743,-0.3131791638\\Version=AM64L-G09RevC.01\\State=2-A'
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.972e-06\\Dipole=-0.0599826,-1.5099074,-0.4555631\\Quadrupole=1.2627421,
-23.9774348,22.7146927,-2.0675814,1.7354925,47.1433652\\PG=CS [SG(C1H1O
1S1),X(C2H8)]\\@
```

BHandHLYP/6-311++G(d,p)

```
1\\1\\GINC-GOMBERG07\\FTS\\UBHandHLYP\\6-311++G(d,p)\\C3H9O1S1(2)\\HMAITKEN\\0
8-May-2012\\1\\#BHandHLYP/6-311++G** opt=(grad,readfc,ts,noeigentest,no
freeze) freq=noraman geom=checkpoint guess=read\\Sulfide\\0,2\\S\\O,1,B1
\\C,1,B2,2,A1\\H,3,B3,1,A2,2,D1,0\\H,3,B4,1,A3,2,D2,0\\H,3,B5,1,A4,2,D3,0\\
C,1,B6,2,A5,3,D4,0\\H,7,B7,1,A6,2,D5,0\\H,7,B8,1,A7,2,D6,0\\H,7,B9,1,A8,2
,D7,0\\C,1,B10,2,A9,3,D8,0\\H,11,B11,1,A10,2,D9,0\\H,11,B12,1,A11,2,D10,0
\\H,11,B13,1,A12,2,D11,0\\B1=1.49033689\\B3=1.0801916\\B4=1.08199443\\B5=1
.08253804\\B7=1.0801916\\B8=1.08199454\\B9=1.08253807\\B10=1.80718251\\B11=
1.08105018\\B12=1.08474415\\B13=1.08105021\\A1=98.75508953\\A2=104.0895464
5\\A3=106.59920525\\A4=108.84518998\\A5=98.75511745\\A6=104.0894802\\A7=106
.59930914\\A8=108.84515703\\A9=109.75462813\\A10=108.53272764\\A11=109.043
5843\\A12=108.53271607\\D1=-67.85727814\\D2=50.14396208\\D3=172.57238981\\D
4=-165.27649015\\D5=67.85701787\\D6=-50.14425041\\D7=-172.57271507\\D8=97.
36172975\\D9=59.76063243\\D10=180.00027501\\D11=-59.76007611\\B2=1.9973416
5\\B6=1.99734199\\Version=AM64L-G09RevC.01\\State=2-A\\HF=-592.9398896\\S2
=0.770238\\S2-1=0.\\S2A=0.750187\\RMSD=3.932e-09\\RMSF=2.054e-06\\Dipole=-0
.0559384,-0.4329687,-1.575703\\Quadrupole=1.4927923,2.4279747,-3.920767
,0.1228759,-0.0064032,-0.0495662\\PG=C01 [X(C3H9O1S1)]\\@
```

ROMP2/6-311G(d,p)//BHandHLYP/6-311G(d,p)

```
1\\1\\GINC-GOMBERG16\\SP\\ROMP2-FC\\6-311G(d,p)\\C3H9O1S1(2)\\HMAITKEN\\04-May
-2012\\0\\#ROMP2/6-311G** geom=checkpoint guess=read\\s_o-t.freq\\0,2\\S
,0,-0.0025281336,-0.1191402595,0.02726806\\O,0,-0.0349705914,-0.2009384
```

```
68,1.5119970271\C,0,1.9702961625,0.0570803563,-0.2416938493\H,0,2.2029
497524,1.0434901834,0.1319463471\H,0,2.4348294229,-0.7130585514,0.3593
689441\H,0,2.1899466703,-0.0365013069,-1.2975473186\C,0,-1.9393127861,
0.2352074728,-0.3173082184\H,0,-2.0955820867,1.2393371573,0.0488099573
\H,0,-2.4947742087,-0.4884590859,0.2640272171\H,0,-2.1256542913,0.1601
233595,-1.3810138363\C,0,-0.0648156521,-1.7835127958,-0.6729962097\H,0
,-0.978914936,-2.2600883117,-0.3473704318\H,0,-0.0407675277,-1.7150393
641,-1.7550893125\H,0,0.7889301029,-2.340633743,-0.3131791638\Version
=AM64L-G09RevC.01\State=2-A'\HF=-591.1101949\MP2=-591.9384922\RMSD=5.5
13e-09\PG=CS [SG(C1H1O1S1),X(C2H8)]\@
```

QCISD/6-311G(d,p)//BHandHLYP/6-311G(d,p)

```
1\1\GINC-GOMBERG16\SP\UQCISD-FC\6-311G(d,p)\C3H9O1S1(2)\HMAITKEN\04-May-2012\0\#QCISD/6-311G** geom=checkpoint guess=read\s_o-t.freq\0,2\
S,0,-0.0025281336,-0.1191402595,0.02726806\O,0,-0.0349705914,-0.200938
468,1.5119970271\C,0,1.9702961625,0.0570803563,-0.2416938493\H,0,2.202
9497524,1.0434901834,0.1319463471\H,0,2.4348294229,-0.7130585514,0.359
3689441\H,0,2.1899466703,-0.0365013069,-1.2975473186\C,0,-1.9393127861
,0.2352074728,-0.3173082184\H,0,-2.0955820867,1.2393371573,0.048809957
3\H,0,-2.4947742087,-0.4884590859,0.2640272171\H,0,-2.1256542913,0.160
1233595,-1.3810138363\C,0,-0.0648156521,-1.7835127958,-0.6729962097\H,
0,-0.978914936,-2.2600883117,-0.3473704318\H,0,-0.0407675277,-1.715039
3641,-1.7550893125\H,0,0.7889301029,-2.340633743,-0.3131791638\Versio
n=AM64L-G09RevC.01\State=2-A'\HF=-591.1220568\MP2=-591.9324074\MP3=-59
1.9746674\MP4D=-591.9960441\MP4DQ=-591.9806331\PUHF=-591.1311835\PMP2-
0=-591.9390855\PMP3-0=-591.9788518\MP4SDQ=-591.9915691\QCISD=-591.9942
874\S2=0.813395\S2-1=0.778824\S2A=0.751737\RMSD=5.851e-09\PG=CS [SG(C1
H1O1S1),X(C2H8)]\@
```

CCSD(T)/6-311G(d,p)//BHandHLYP/6-311G(d,p)

```
1\1\GINC-GOMBERG16\SP\UCCSD(T)-FC\6-311G(d,p)\C3H9O1S1(2)\HMAITKEN\04-May-2012\0\#CCSD(T)/6-311G** geom=checkpoint guess=read\s_o-t.freq\0,2\
S,0,-0.0025281336,-0.1191402595,0.02726806\O,0,-0.0349705914,-0.20
0938468,1.5119970271\C,0,1.9702961625,0.0570803563,-0.2416938493\H,0,2
.2029497524,1.0434901834,0.1319463471\H,0,2.4348294229,-0.7130585514,0
.3593689441\H,0,2.1899466703,-0.0365013069,-1.2975473186\C,0,-1.939312
7861,0.2352074728,-0.3173082184\H,0,-2.0955820867,1.2393371573,0.04880
99573\H,0,-2.4947742087,-0.4884590859,0.2640272171\H,0,-2.1256542913,0
.1601233595,-1.3810138363\C,0,-0.0648156521,-1.7835127958,-0.672996209
7\H,0,-0.978914936,-2.2600883117,-0.3473704318\H,0,-0.0407675277,-1.71
50393641,-1.7550893125\H,0,0.7889301029,-2.340633743,-0.3131791638\Ve
rsion=AM64L-G09RevC.01\State=2-A'\HF=-591.1220568\MP2=-591.9324074\MP3
=-591.9746674\MP4D=-591.9960441\MP4DQ=-591.9806331\PUHF=-591.1311835\P
MP2-0=-591.9390855\PMP3-0=-591.9788518\MP4SDQ=-591.9915691\CCSD=-591.9
913059\CCSD(T)=-592.0227855\S2=0.813395\S2-1=0.778824\S2A=0.751737\RMS
D=5.851e-09\PG=CS [SG(C1H1O1S1),X(C2H8)]\@
```

Transition state 1 (n = 2)

B3LYP/6-31G(d)

```
1\1\GINC-V1460\FTS\UB3LYP\Gen\C3H9O2S1(2)\HMA563\04-Apr-2012\0\#B3LYP
/gen 6D INT(grid=ultrafine) OPT=(TS,calcfc,noeigentest,maxcyc=200) IOP
(2/17=4) Freq=noraman maxdisk=268435456\s_o2-t.freq\0,2\S,0.00627994
31,-0.012388986,-0.0123517989\O,0.0010616819,-0.0726433115,1.507614755
```


9\ C, 1.9686108365, 0.0578368475, 0.0454333907\ H, 2.34827957, 0.0190005006, -
0.9772166757\ H, 2.2515678563, 0.9985443117, 0.5185404065\ H, 2.3296212851, -
0.7864497598, 0.6355807002\ O, 0.0297748709, 1.1664597627, -0.9734518379\ C,
-1.9556885301, 0.1266149981, 0.0343661143\ H, -2.2006190583, 1.0783575045, 0.
.5068749807\ H, -2.3545475871, -0.7005222488, 0.6239853726\ H, -2.3359085133
, 0.104784409, -0.9883146637\ C, -0.0547370244, -1.6622175714, -0.8370575841
\ H, -0.5861374181, -1.5353967777, -1.782248584\ H, 0.9556380523, -2.03361916
8, -1.0108588073\ H, -0.6045085296, -2.3367454055, -0.177733125\ \Version=EM
64L-G09RevA.02\ State=2-A\ HF=-668.1712723\ S2=0.754951\ S2-1=0.\ S2A=0.750
016\ RMSD=3.895e-09\ RMSF=5.640e-06\ Dipole=-0.0349481, -1.0581045, -0.5288
889\ Quadrupole=2.2135654, 0.5873076, -2.800873, -0.0178959, 0.0624491, 2.25
48971\ PG=C01 [X(C3H9O2S1)]\ \@

BHandHLYP/6-311G(d,p)

1\ 1\ GINC-GOMBERG05\ FTS\ UBHandHLYP\ 6-311G(d,p)\ C3H9O2S1(2)\ HMAITKEN\ 18-
Apr-2012\ 0\ \#BHandHLYP/6-311G** 6D INT(grid=ultrafine) OPT=(TS,calcfc,
noeigentest,maxcyc=200) IOP(2/17=4) Freq=noraman\ \s_o2-t.freq\ \0,2\ S,0
.0015329094, 0.0515304683, -0.1633267923\ O, -0.0503904262, -0.0107598854, 1.
.4512864189\ C, 1.8685651892, -0.0056767622, 0.1334959216\ H, 2.3332700509, -
0.0398368668, -0.8426024267\ H, 2.158270118, 0.9106498157, 0.6294880577\ H, 2.
.1589217828, -0.8631707333, 0.728982932\ O, 0.0723748401, 1.1693161466, -1.1
114511954\ C, -1.8794341567, 0.136833847, 0.0204767372\ H, -2.1284692339, 1.0
742875252, 0.4986999584\ H, -2.2698412983, -0.6940025105, 0.5962045039\ H, -2
.2850067368, 0.1343433643, -0.9822240604\ C, -0.040905884, -1.6217777914, -0
.8690314573\ H, -0.9152567154, -1.7111850013, -1.4970370559\ H, 0.859701144,
-1.7780487007, -1.4446968751\ H, -0.091612751, -2.3233979817, -0.0460490276
\ \Version=AM64L-G09RevC.01\ State=2-A\ HF=-668.0752441\ S2=0.755685\ S2-1=
0.\ S2A=0.750025\ RMSD=9.910e-09\ RMSF=3.469e-05\ Dipole=-0.052398, -1.3911
535, -0.0025242\ Quadrupole=2.6528753, -0.1967163, -2.4561591, -0.2052764, 0
.2786015, 3.1998987\ PG=C01 [X(C3H9O2S1)]\ \@

BHandHLYP/6-311++G(d,p)

1\ 1\ GINC-GOMBERG02\ FTS\ UBHandHLYP\ 6-311++G(d,p)\ C3H9O2S1(2)\ HMAITKEN\ 0
8-May-2012\ 1\ \#BHandHLYP/6-311++G** opt=(grad,readfc,ts,noeigentest,no
freeze) freq=noraman geom=checkpoint guess=read\ \Sulfoxide\ \0,2\ S\ O,1,
B1\ C,1,B2,2,A1\ H,3,B3,1,A2,2,D1,0\ H,3,B4,1,A3,2,D2,0\ H,3,B5,1,A4,2,D3,
0\ O,1,B6,2,A5,3,D4,0\ C,1,B7,7,A6,3,D5,0\ H,8,B8,1,A7,7,D6,0\ H,8,B9,1,A8
,7,D7,0\ H,8,B10,1,A9,7,D8,0\ C,1,B11,7,A10,3,D9,0\ H,12,B12,1,A11,7,D10,
0\ H,12,B13,1,A12,7,D11,0\ H,12,B14,1,A13,7,D12,0\ \B1=1.62547816\ B3=1.08
175635\ B4=1.08158991\ B5=1.08369065\ B6=1.4702212\ B8=1.0815701\ B9=1.0836
774\ B10=1.08176396\ B11=1.8172806\ B12=1.08026861\ B13=1.0802876\ B14=1.08
296085\ A1=82.61042903\ A2=106.38304215\ A3=108.14345573\ A4=111.99518248\
A5=132.68567336\ A6=94.37274176\ A7=108.15017669\ A8=112.02158143\ A9=106.
33771342\ A10=116.43417689\ A11=108.56881755\ A12=108.55169507\ A13=107.71
126223\ D1=176.13333086\ D2=-66.9242338\ D3=54.86670721\ D4=-89.17237059\ D
5=167.94566832\ D6=-65.56067344\ D7=172.61243047\ D8=51.36643138\ D9=-96.0
3074743\ D10=-60.31751535\ D11=60.17768756\ D12=179.92450309\ B2=1.8879690
5\ B7=1.88854899\ \Version=AM64L-G09RevC.01\ State=2-A\ HF=-668.0793013\ S2
=0.756064\ S2-1=0.\ S2A=0.750029\ RMSD=6.082e-09\ RMSF=3.036e-05\ Dipole=-0
.0200328, -1.3900601, 0.0636869\ Quadrupole=2.8338362, 0.0538072, -2.887643
4, -0.040548, 0.0481349, 3.2361376\ PG=C01 [X(C3H9O2S1)]\ \@

ROMP2/6-311G(d,p)//BHandHLYP/6-311G(d,p)

1\ 1\ GINC-GOMBERG06\ SP\ ROMP2-FC\ 6-311G(d,p)\ C3H9O2S1(2)\ HMAITKEN\ 04-May
-2012\ 0\ \#ROMP2/6-311G** geom=checkpoint guess=read\ \s_o2-t.freq\ \0,2\
S,0,0.0019956437, 0.0503665044, -0.1626013123\ O, 0, -0.0499276919, -0.01192


```
38492,1.4520118989\C,0,1.8690279236,-0.006840726,0.1342214016\H,0,2.33
37327852,-0.0410008306,-0.8418769467\H,0,2.1587328523,0.9094858519,0.6
302135377\H,0,2.1593845171,-0.8643346972,0.7297084119\O,0,0.0728375744
,1.1681521827,-1.1107257154\C,0,-1.8789714223,0.1356698832,0.021202217
1\H,0,-2.1280064996,1.0731235614,0.4994254383\H,0,-2.269378564,-0.6951
664743,0.5969299839\H,0,-2.2845440025,0.1331794005,-0.9814985804\C,0,-
0.0404431497,-1.6229417552,-0.8683059774\H,0,-0.914793981,-1.712348965
1,-1.4963115759\H,0,0.8601638783,-1.7792126645,-1.4439713951\H,0,-0.09
11500167,-2.3245619455,-0.0453235476\\Version=AM64L-G09RevC.01\State=2
-A\HF=-665.9338468\MP2=-666.9374707\RMSD=7.205e-09\PG=C01 [X(C3H9O2S1)
]\@
```

QCISD/6-311G(d,p)//BHandHLYP/6-311G(d,p)

```
1\1\GINC-GOMBERG06\SP\UQCISD-FC\6-311G(d,p)\C3H9O2S1(2)\HMAITKEN\04-May-2012\0\#QCISD/6-311G** geom=checkpoint guess=read\\s_o2-t.freq\
\S,0,0.0019956437,0.0503665044,-0.1626013123\O,0,-0.0499276919,-0.0119
238492,1.4520118989\C,0,1.8690279236,-0.006840726,0.1342214016\H,0,2.3
337327852,-0.0410008306,-0.8418769467\H,0,2.1587328523,0.9094858519,0.6
6302135377\H,0,2.1593845171,-0.8643346972,0.7297084119\O,0,0.072837574
4,1.1681521827,-1.1107257154\C,0,-1.8789714223,0.1356698832,0.02120221
71\H,0,-2.1280064996,1.0731235614,0.4994254383\H,0,-2.269378564,-0.695
1664743,0.5969299839\H,0,-2.2845440025,0.1331794005,-0.9814985804\C,0,-
0.0404431497,-1.6229417552,-0.8683059774\H,0,-0.914793981,-1.71234896
51,-1.4963115759\H,0,0.8601638783,-1.7792126645,-1.4439713951\H,0,-0.0
911500167,-2.3245619455,-0.0453235476\\Version=AM64L-G09RevC.01\State=
2-A\HF=-665.9388226\MP2=-666.9374057\MP3=-666.976799\MP4D=-667.0013277
\MP4DQ=-666.982337\PUHF=-665.9422769\MP2-0=-666.9396025\MP3-0=-666.9
783095\MP4SDQ=-666.996667\QCISD=-667.0034467\S2=0.759469\S2-1=0.752544
\S2A=0.750072\RMSD=4.439e-09\PG=C01 [X(C3H9O2S1)]\@
```

CCSD(T)/6-311G(d,p)//BHandHLYP/6-311G(d,p)

```
1\1\GINC-GOMBERG05\SP\UCCSD(T)-FC\6-311G(d,p)\C3H9O2S1(2)\HMAITKEN\05-May-2012\0\#CCSD(T)/6-311G** geom=checkpoint guess=read\\s_o2-t.freq\
\S,0,0.0019956437,0.0503665044,-0.1626013123\O,0,-0.0499276919,-0.0
0119238492,1.4520118989\C,0,1.8690279236,-0.006840726,0.1342214016\H,0
,2.3337327852,-0.0410008306,-0.8418769467\H,0,2.1587328523,0.909485851
9,0.6302135377\H,0,2.1593845171,-0.8643346972,0.7297084119\O,0,0.07283
75744,1.1681521827,-1.1107257154\C,0,-1.8789714223,0.1356698832,0.0212
022171\H,0,-2.1280064996,1.0731235614,0.4994254383\H,0,-2.269378564,-0
.6951664743,0.5969299839\H,0,-2.2845440025,0.1331794005,-0.9814985804\
C,0,-0.0404431497,-1.6229417552,-0.8683059774\H,0,-0.914793981,-1.7123
489651,-1.4963115759\H,0,0.8601638783,-1.7792126645,-1.4439713951\H,0,
-0.0911500167,-2.3245619455,-0.0453235476\\Version=AM64L-G09RevC.01\St
ate=2-A\HF=-665.9388226\MP2=-666.9374057\MP3=-666.976799\MP4D=-667.001
3277\MP4DQ=-666.982337\PUHF=-665.9422769\MP2-0=-666.9396025\MP3-0=-6
66.9783095\MP4SDQ=-666.996667\CCSD=-666.9974175\CCSD(T)=-667.0374712\S
2=0.759469\S2-1=0.752544\S2A=0.750072\RMSD=4.439e-09\PG=C01 [X(C3H9O2S
1)]\@
```

Transition state 3 (n = 0; R = Me)

B3LYP/6-31G(d)

```
1\1\GINC-X89\FTS\UB3LYP\Gen\C5H11S1(2)\HMA563\29-Jun-2011\0\#B3LYP/ge
n 6D INT(grid=ultrafine) OPT=(TS,calcfc,noeigentest,maxcyc=200) IOP(2/
17=4) Freq=noraman maxdisk=1610612736\\sch2t-6.freq\0,2\S,-0.74420687
25,-0.5339321368,-0.2283671228\C,-0.0476833694,1.1659228636,0.00879062
```

47\C,1.459519454,1.106584655,-0.2360636161\C,1.9881942151,-0.172260369
6,0.4309941421\C,1.1273416975,-1.325190481,-0.0528029918\H,1.949935011
1,2.0059135705,0.15668507\H,1.659036601,1.0672294928,-1.3145286676\H,3
.0495117649,-0.3331452081,0.1953974605\H,1.9088281192,-0.0767101937,1.
5215621009\H,1.375724504,-1.6686712735,-1.0601022924\H,1.0527129522,-2
.169372762,0.6332126217\C,-2.7271004482,0.1355577828,0.248993153\H,-2.
6982567301,0.5545450137,1.2545425942\H,-2.9824429459,0.8666564476,-0.5
193032536\H,-3.3249059068,-0.7718516115,0.1850247414\H,-0.2664011792,1
.4942352097,1.0313684259\H,-0.5537618669,1.8454620004,-0.6823039902\\V
ersion=EM64L-G09RevA.02\State=2-A\HF=-595.259212\S2=0.762249\S2-1=0.\S
2A=0.750061\RMSD=4.559e-09\RMSF=8.064e-06\Dipole=0.4166337,0.3940892,0
.1805165\Quadrupole=0.3782215,0.5577782,-0.9359997,-0.6365106,-0.35433
06,-0.2150086\PG=C01 [X(C5H11S1)]\\@

Transition state 3 (n = 0; R = Et)

B3LYP/6-31G(d)

1\1\GINC-GOMBERG03\FTS\UB3LYP\Gen\C6H13S1(2)\HMAITKEN\25-Sep-2011\0\\#
B3LYP/gen 6D INT(grid=ultrafine) OPT=(TS,calcfc,noeigentest,maxcyc=200
) IOP(2/17=4) Freq=noraman\\sch2-et-t.freq\\0,2\S,-0.0004953484,-0.039
8817501,-0.0111753524\C,-0.0057717681,-0.0378457232,1.8411179236\C,1.4
40172884,-0.0022919783,2.334115483\C,2.2600719296,-0.9692978106,1.4659
809049\C,2.0029959409,-0.6151013562,0.0155996176\H,1.4902952955,-0.266
911934,3.3977759677\H,1.8418942042,1.0136296472,2.2288528905\H,3.32958
32383,-0.9094546927,1.7144111414\H,1.939509547,-2.000407093,1.66327336
28\H,2.5354103321,0.272858902,-0.3318211668\H,2.0960684316,-1.43469371
38,-0.6964987335\C,-2.1185568964,-0.0126098198,-0.1112377319\H,-2.4398
323677,-0.8806112991,0.4684272824\H,-2.3806666743,0.921002389,0.392990
293\H,-0.5154661058,-0.9426765856,2.1925429815\H,-0.5771873673,0.82867
26316,2.1855655762\C,-2.5096533248,-0.0604509146,-1.5687505225\H,-2.08
93661396,0.7872964751,-2.1218418827\H,-2.1561203631,-0.9819733077,-2.0
448555609\H,-3.6021452576,-0.0239796144,-1.6864658153\\Version=AM64L-G
09RevB.01\State=2-A\HF=-634.5758167\S2=0.763261\S2-1=0.\S2A=0.750067\R
MSD=4.536e-09\RMSF=4.801e-06\Dipole=0.0499075,-0.1269686,0.4859531\Qua
drupole=1.2306036,-1.2484345,0.0178309,-0.3294243,0.3889345,0.3309101\
PG=C01 [X(C6H13S1)]\\@

Transition state 3 (n = 0; R = t-Bu)

B3LYP/6-31G(d)

1\1\GINC-X65\FTS\UB3LYP\Gen\C8H17S1(2)\HMA563\26-Jul-2011\0\\#B3LYP/ge
n 6D INT(grid=ultrafine) OPT=(TS,calcfc,noeigentest,maxcyc=200) IOP(2/
17=4) Freq=noraman maxdisk=1342177280\\sch2ttb.freq\\0,2\S,-0.09519825
7,-0.1538413614,0.0962404158\C,0.0462875009,-0.2595942256,1.9381200843
\C,1.5065660238,-0.0414730597,2.3360543996\C,2.4002715434,-0.881463657
4,1.4097607926\C,2.0654377115,-0.5355081862,-0.020500362\H,1.656052062
9,-0.3089779447,3.3902265721\H,1.7630850515,1.0201020468,2.2268514694\
H,3.4626483819,-0.6964462705,1.631359644\H,2.2154612361,-1.9478153176,
1.5931202291\H,2.449604392,0.4206963935,-0.3757205958\H,2.1670142027,-
1.3280340398,-0.7594033498\C,-2.2103729809,-0.0261575167,-0.0470367247
\H,-0.2955226762,-1.245787709,2.2710391621\H,-0.6024222089,0.496095939
8,2.3886571916\C,-2.8210711867,-1.1967927717,0.7057826009\H,-2.4262384
825,-2.1528503895,0.3458396\H,-2.6426283757,-1.1341141827,1.7847052821
\H,-3.9132899952,-1.2096631112,0.560035668\C,-2.6280869981,1.3294073308
2,0.5008562308\H,-2.4227266708,1.4264403573,1.572802462\H,-2.118336870
6,2.1455130778,-0.0210614626\H,-3.7131827578,1.4709477508,0.3684453574
\C,-2.417374586,-0.1300782662,-1.5501900377\H,-1.8912179185,0.67012463
27,-2.0829616459\H,-2.0614943321,-1.0907315487,-1.937784753\H,-3.48739
51173,-0.0443565439,-1.7920985099\\Version=EM64L-G09RevA.02\State=2-A\

HF=-713.2069822\S2=0.767067\S2-1=0.\S2A=0.750091\RMSD=8.337e-09\RMSF=3
.254e-06\Dipole=-0.0507464,-0.0658223,0.4277359\Quadrupole=1.4865683,-
1.4476198,-0.0389486,-0.362833,1.0015674,-0.026252\PG=C01 [X(C8H17S1)]
\@

Transition state 3 (n = 0; R = Bn)

B3LYP/6-31G(d)

1\1\GINC-GOMBERG01\FTS\UB3LYP\Gen\C11H15S1(2)\HMAITKEN\25-Sep-2011\0\@
#B3LYP/gen 6D INT(grid=ultrafine) OPT=(TS,calcfc,noeigentest,maxcyc=200) IOP(2/17=4) Freq=noraman\sch2-bn-t.freq\0,2\S,0.0154385066,-0.082
8432668,-0.0330400551\C,-0.0124326029,-0.052718644,1.8171768272\C,1.41
94594828,0.0472296899,2.3421086054\C,2.303089951,-0.9399591339,1.56198
95376\C,2.1406597884,-0.6664746177,0.0879052268\H,1.4424455944,-0.1571
727741,3.4201784934\H,1.7952448903,1.0677778068,2.1944989924\H,3.35377
22259,-0.8427370001,1.8760324318\H,1.9942615388,-1.9680509079,1.790817
8042\H,2.6292989996,0.2339147071,-0.2850945493\H,2.2370566486,-1.51071
87781,-0.5912853587\C,-2.0521677733,-0.079858416,-0.1848177016\H,-2.36
08580632,-0.9693965945,0.3665482282\H,-2.329147195,0.8323978411,0.3474
439304\H,-0.4935823004,-0.9701914472,2.1775410255\H,-0.619344032,0.797
4809921,2.1428997436\C,-2.4527338529,-0.0853218904,-1.6062557229\C,-2.
6534365733,-1.2943921783,-2.2955690537\C,-2.6059046456,1.1176044847,-2.
.3182153309\C,-3.0070888265,-1.3008702047,-3.643316756\H,-2.5316493008
, -2.2347897208,-1.7628589011\C,-2.9599504949,1.1127319527,-3.665771382
5\H,-2.4459489655,2.0622702246,-1.8035736206\C,-3.1630541443,-0.096937
4485,-4.3347463163\H,-3.1631837752,-2.2469089988,-4.1555878113\H,-3.07
89473095,2.054448751,-4.1955964244\H,-3.4410724455,-0.1013079566,-5.38
53087513\Version=AM64L-G09RevB.01\State=2-A\HF=-826.3172523\S2=0.7658
99\S2-1=0.\S2A=0.75013\RMSD=8.757e-09\RMSF=3.915e-06\Dipole=0.1409758,
-0.1074885,0.5992082\Quadrupole=-2.5510437,-0.349734,2.9007778,-0.4115
063,2.529585,-0.0145535\PG=C01 [X(C11H15S1)]\@

Transition state 3 (n = 1; R = Me)

B3LYP/6-31G(d)

1\1\GINC-X90\FTS\UB3LYP\Gen\C5H11O1S1(2)\HMA563\29-Jun-2011\0\@#B3LYP/
gen 6D INT(grid=ultrafine) OPT=(TS,calcfc,noeigentest,maxcyc=200) IOP(2/17=4) Freq=noraman maxdisk=1610612736\sch2ot-6.freq\0,2\S,-0.66087
62816,-0.3490190351,-0.2057658559\C,0.1707613494,1.2620405963,0.257119
0524\C,1.6916177225,1.1509474103,0.0817124389\C,2.0838480938,-0.335916
2113,0.1600141661\C,1.1177742088,-1.0771031886,-0.7429208096\H,2.21391
94487,1.7496130832,0.8363573145\H,1.981208856,1.5472897596,-0.89977055
24\H,3.1300882498,-0.4826744985,-0.1405987311\H,1.9750822741,-0.705064
2566,1.186181551\H,1.2579363979,-0.8502113911,-1.8054227342\H,1.024389
862,-2.1513901939,-0.579545452\O,-0.9152770648,-1.160783811,1.04599294
52\C,-2.5754378266,0.5745042657,-0.3387365403\H,-3.2356053971,-0.28930
08837,-0.3938581508\H,-2.6913351278,1.1337905772,0.5902488976\H,-2.603
3326727,1.1984720713,-1.2331607995\H,-0.1244934118,1.3967397935,1.3027
240106\H,-0.2781296807,2.0614309128,-0.3387157506\Version=EM64L-G09Re
vA.02\State=2-A\HF=-670.4338333\S2=0.761876\S2-1=0.\S2A=0.750067\RMSD=
7.202e-09\RMSF=1.539e-06\Dipole=0.6800368,0.9556213,-0.8056358\Quadrup
ole=0.9732369,-0.1524932,-0.8207437,-1.5355592,1.5600773,2.434435\PG=C
01 [X(C5H11O1S1)]\@

Transition state 3 (n = 1; R = t-Bu)

B3LYP/6-31G(d)

1\1\GINC-X149\FTS\UB3LYP\Gen\C8H17O1S1(2)\HMA563\26-Jul-2011\0\@#B3LYP

```
/gen 6D INT(grid=ultrafine) OPT=(TS,calcfc,noeigentest,maxcyc=200) IOP
(2/17=4) Freq=noraman maxdisk=1342177280\\sch2ottb.freq\\0,2\\S,-0.0825
675464,-0.0346306965,0.053700606\\C,0.0547488754,-0.0563138281,1.920583
2916\\C,1.5129926945,0.1037043978,2.363222822\\C,2.4388295365,-0.5500455
186,1.3222507194\\C,2.1016841709,0.0465648692,-0.0190679132\\H,1.6530309
951,-0.3313060595,3.3602717874\\H,1.7610318684,1.1704186872,2.443065376
7\\H,3.4923291178,-0.3873380923,1.5962060013\\H,2.2690126826,-1.63294878
42,1.2975310015\\H,2.3648602541,1.09983338,-0.1396828726\\H,2.2905554894
,-0.5491817714,-0.9097600031\\O,-0.227993303,-1.4763161716,-0.405661548
5\\C,-2.1032588159,0.5719070142,-0.0607805337\\H,-0.3467417483,-1.040836
8842,2.1808960584\\H,-0.5952082996,0.7145281402,2.3403277654\\C,-2.92582
32574,-0.4031475213,0.7642968292\\H,-2.6622517391,-1.4348390813,0.50899
98077\\H,-2.7877901524,-0.2599162301,1.8417341584\\H,-3.9978824237,-0.26
60431468,0.5530264157\\C,-2.1779850502,2.0171582053,0.4021365637\\H,-2.0
001267356,2.1267666685,1.4782044255\\H,-1.4569296481,2.6489711331,-0.13
17214969\\H,-3.1788967202,2.4266929506,0.2011606284\\C,-2.3612212536,0.4
20171096,-1.5530316815\\H,-1.7409284267,1.1070453057,-2.1418356431\\H,-2
.1507875462,-0.6022696325,-1.8806079326\\H,-3.4134724543,0.6458626098,-
1.7788715582\\Version=EM64L-G09RevA.02\\State=2-A\\HF=-788.3836754\\S2=0.
766961\\S2-1=0.\\S2A=0.750104\\RMSD=2.902e-09\\RMSF=6.977e-06\\Dipole=0.035
3145,1.0246986,0.7955968\\Quadrupole=2.7927046,-3.3294607,0.5367561,-0.
1949421,1.2422918,-2.2486777\\PG=C01 [X(C8H17O1S1)]\\@
```

Transition state 3 (n = 1; R = Me)

B3LYP/6-31G(d)

```
1\\1\\GINC-X79\\FTS\\UB3LYP\\Gen\\C5H11O2S1(2)\\HMA563\\30-Jun-2011\\0\\#B3LYP/
gen 6D INT(grid=ultrafine) OPT=(TS,calcfc,noeigentest,maxcyc=200) IOP(
2/17=4) Freq=noraman maxdisk=2684354560\\sch2o2t.freq\\0,2\\S,-0.579023
7368,-0.195978387,-0.0329125905\\C,0.4396229025,1.3833297129,-0.0423693
9\\C,1.91279201,1.0369819926,0.1575448197\\C,2.152771416,-0.4006908344,-
0.3553528475\\C,1.0667463486,-1.2658682723,0.2569993353\\H,2.1626122716,
1.0822990609,1.2241646824\\H,2.5504208899,1.7625497327,-0.3588534685\\H,
2.0882123257,-0.4309404705,-1.4496704516\\H,3.1544261844,-0.7439658247,
-0.0699678598\\H,0.9174965745,-2.2320162415,-0.2230905797\\H,1.208837574
8,-1.3919289242,1.3320467394\\O,-1.1270561632,-0.655400418,1.3129285258
\\C,-2.2804228875,0.7894830273,-0.2945045212\\H,-2.2000288335,1.35883898
32,-1.2216213687\\H,-3.0779714715,0.0502625005,-0.3694088746\\H,-2.44040
15744,1.4409498406,0.5659223022\\H,0.0145805976,2.0221334,0.7348385601\\
H,0.2336110608,1.8226868561,-1.0222294583\\O,-0.7491904896,-0.797268734
3,-1.4163225543\\Version=EM64L-G09RevA.02\\State=2-A\\HF=-745.5983165\\S2
=0.755066\\S2-1=0.\\S2A=0.750018\\RMSD=4.560e-09\\RMSF=5.250e-05\\Dipole=0.
8410606,0.9884027,0.0429243\\Quadrupole=1.771593,1.4409019,-3.2124949,-
1.5158686,0.704862,-0.3680953\\PG=C01 [X(C5H11O2S1)]\\@
```

Transition state 3 (n = 2; R = t-Bu)

B3LYP/6-31G(d)

```
1\\1\\GINC-X126\\FTS\\UB3LYP\\Gen\\C8H17O2S1(2)\\HMA563\\26-Jul-2011\\0\\#B3LYP
/gen 6D INT(grid=ultrafine) OPT=(TS,calcfc,noeigentest,maxcyc=200) IOP
(2/17=4) Freq=noraman maxdisk=1342177280\\sch2o2ttb.freq\\0,2\\S,0.0289
337326,0.0054190266,0.0550197831\\C,0.1048912443,0.0800683683,1.9404907
957\\C,1.5596455463,-0.0080014578,2.3879512996\\C,2.4494497674,0.6424722
228,1.3080689388\\C,2.0700758577,0.0033180287,-0.01026296\\H,1.849362993
5,-1.0590024707,2.5071246708\\H,1.6828601996,0.4780193829,3.3623302741\\
H,2.273112196,1.7245325296,1.2729016772\\H,3.5093938499,0.484611572,1.5
449844606\\H,2.3508036632,0.5592712244,-0.9026992529\\H,2.4016738726,-1.
0335799253,-0.0761012548\\O,0.0514814623,-1.3815213067,-0.5639212149\\C,
-2.0719475029,-0.03198221,-0.0945476676\\H,-0.5261204433,-0.7261236754,
2.3147049125\\H,-0.3459405529,1.0436075622,2.1852660962\\O,0.0369896492,
```

1.3858939762,-0.5675783743\C,-2.6489316255,1.1855586899,0.6315130885\H
, -2.4931366698,1.1472528748,1.7152421265\H,-2.2323208621,2.1204185305,
0.2498150893\H,-3.7378172855,1.20720974,0.4730860976\C,-2.6092487659,-
1.3322050291,0.5059665132\H,-2.2381952061,-2.208717997,-0.0291220007\H
, -2.3627688831,-1.447723036,1.5676767859\H,-3.7078243827,-1.326613337,
0.4401386928\C,-2.3755817587,0.0378939723,-1.5921111868\H,-2.002609336
6,0.9646942583,-2.0349133743\H,-1.9373123462,-0.8063456294,-2.13088959
78\H,-3.4651381032,0.0040027501,-1.7406965732\\Version=EM64L-G09RevA.0
2\State=2-A\HF=-863.5370662\S2=0.755374\S2-1=0.\S2A=0.750022\RMSD=1.64
2e-09\RMSF=1.152e-05\Dipole=0.0250401,0.0220548,1.1596286\Quadrupole=3
.2521577,-3.7286343,0.4764765,0.1527096,1.8077263,0.1013426\PG=C01 [X(
C8H17O2S1)]\@