

# **Group Additivity using the THERM Program**

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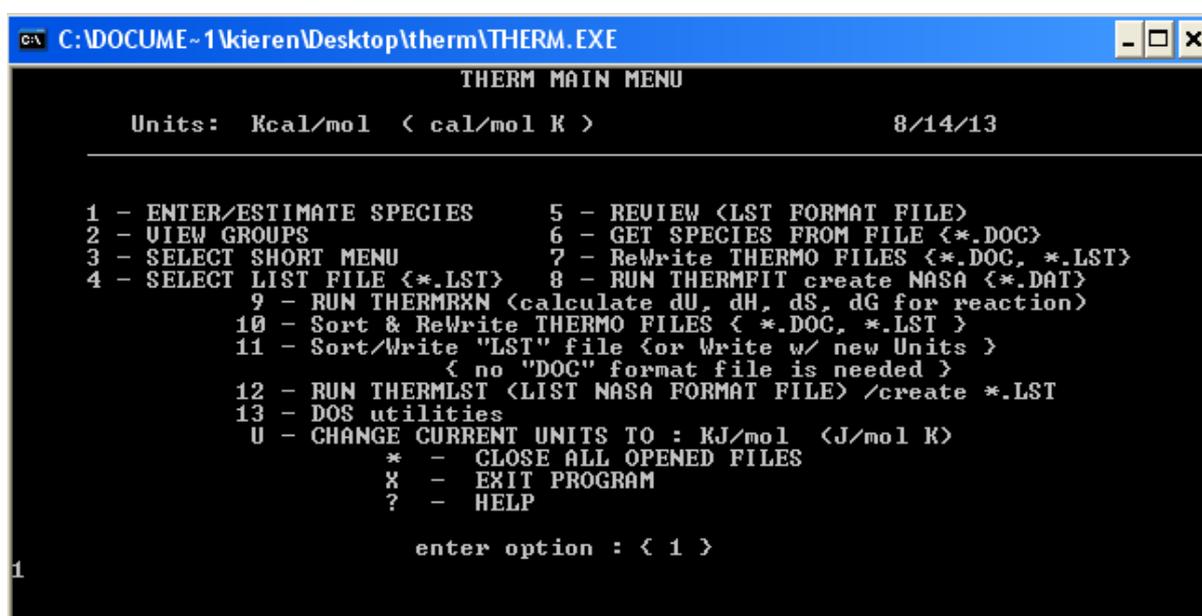
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*Princeton University*

## Ethane and the Ethyl Radical

We will introduce you to the general features of the THERM software package by estimating thermochemical parameters for ethane and the ethyl radical. Ethane is effectively the simplest molecule to describe using the concepts of group additivity as it is a symmetric molecule consisting of two identical groups.

1. Double click on the 'therm.exe' file in the 'THERM' folder you have been given.
2. When the program starts, it will enter full screen mode – press Alt+Enter to restore it to window mode then and press enter to view the main menu of the programme.



```
C:\DOCUMENTS AND SETTINGS\kieren\Desktop\therm\THERM.EXE
THERM MAIN MENU
Units: Kcal/mol < cal/mol K > 8/14/13
1 - ENTER/ESTIMATE SPECIES          5 - REVIEW <LST FORMAT FILE>
2 - VIEW GROUPS                    6 - GET SPECIES FROM FILE <*.DOC>
3 - SELECT SHORT MENU              7 - ReWrite THERMO FILES <*.DOC, *.LST>
4 - SELECT LIST FILE <*.LST>      8 - RUN THERMFIT create NASA <*.DAT>
    9 - RUN THERMRXN <calculate dU, dH, dS, dG for reaction>
   10 - Sort & ReWrite THERMO FILES < *.DOC, *.LST >
   11 - Sort/Write "LST" file <or Write w/ new Units >
        < no "DOC" format file is needed >
   12 - RUN THERMLST <LIST NASA FORMAT FILE> /create *.LST
   13 - DOS utilities
    U - CHANGE CURRENT UNITS TO : KJ/mol <J/mol K>
        * - CLOSE ALL OPENED FILES
        X - EXIT PROGRAM
        ? - HELP
enter option : < 1 >
```

3. On the main menu there are several options which can be selected by typing the relevant number and pressing enter.
4. In this case, press 1 and hit enter so that we can estimate thermochemistry for a new species.
5. You will now be asked to enter the species name, type C2H6 to represent ethane and hit enter:



```
C:\DOCUMENTS AND SETTINGS\kieren\Desktop\therm\THERM.EXE
Enter species name <ID>
9 characters maximum
< "Q" return to opening menu >
C2H6
```

6. Now you will be asked to enter the molecular formula for ethane, type C2H6 and press enter.

```

C:\> C:\DOCUME~1\kieren\Desktop\therm\THERM.EXE

enter the elemental formula for this species
< example: for PHENOL enter " C6H5OH " >
<           for TOLUENE enter " C6H5CH3 " >
<           for CHLOROPHENOL enter " C6H4CLOH " >

      4 ELEMENTS MAXIMUM : 70 CHARACTERS MAX

THE FOLLOWING ELEMENTS ARE DEFINED:
C  H  O  CL  S  N  F  P  I  BR
B  SI  LI

ALL OTHER ELEMENTS OR NON-NUMERIC CHARACTERS
      WILL BE IGNORED !

enter formula here: <Q=QUIT>
C2H6_
  
```

7. THERM will now reiterate your input as follows, press enter to proceed.

```

C:\> C:\DOCUME~1\kieren\Desktop\therm\THERM.EXE

FORMULA ENTERED :
C2H6

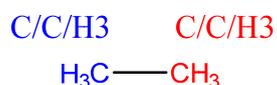
      ELEMENTAL COMPOSITION:

C                2
H                6
                 0
                 0

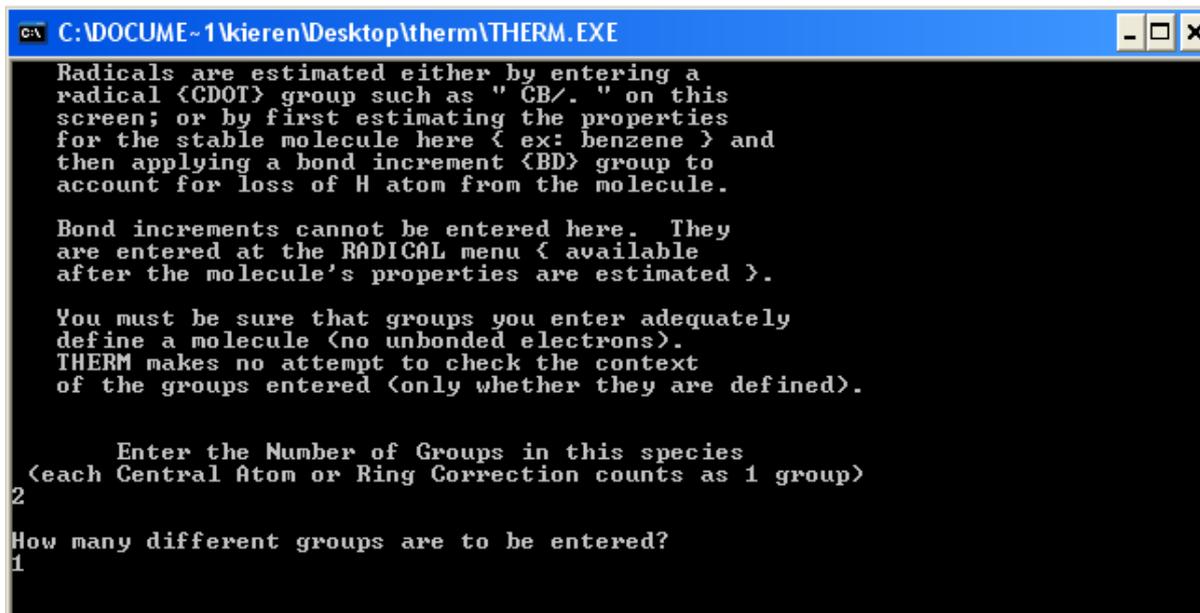
number of Atoms for This Species =           8

      IF THIS IS INCORRECT ENTER " Q "
      TO BEGIN AGAIN
      OTHERWISE HIT RETURN TO CONTINUE
  
```

8. You will now be asked to enter the total number of groups in your molecule. In the case of ethane, there are a total of two groups as seen below. Type 2 and press enter.



9. You will now be asked to enter the number of different groups in your molecule, type 1 and press enter.



```
C:\DOCUME~1\kieren\Desktop\therm\THERM.EXE
Radicals are estimated either by entering a
radical <CDOT> group such as " CB/." on this
screen; or by first estimating the properties
for the stable molecule here < ex: benzene > and
then applying a bond increment <BD> group to
account for loss of H atom from the molecule.

Bond increments cannot be entered here. They
are entered at the RADICAL menu < available
after the molecule's properties are estimated >.

You must be sure that groups you enter adequately
define a molecule <no unbonded electrons>.
THERM makes no attempt to check the context
of the groups entered <only whether they are defined>.

Enter the Number of Groups in this species
<each Central Atom or Ring Correction counts as 1 group>
2
How many different groups are to be entered?
1
```

10. You are now prompted to enter the total number of rotors in the species. All non-linear molecules, such as ethane, have  $3N-6$  vibrational degrees of freedom, but in the case of ethane, one vibration corresponds to internal rotation about the C–C axis of the molecule. At infinite temperature, the contribution of a vibrational mode to the constant pressure heat capacity is  $R$ , where  $C_p(T = \infty) = C_v(T = \infty) + R$ , where  $C_v(T = \infty) = C_{\text{TRANS}} + C_{\text{ROT}} + C_{\text{VIB}}$  and  $C_{\text{TRANS}} = 3/2 R$ ,  $C_{\text{ROT}} = 3/2 R$ , and  $C_{\text{VIB}} = (3N-6)R$ . However, an internal rotation contributes only  $R/2$  at infinite temperature. THERM will therefore correct  $C_p(T = \infty)$  accordingly based on the user input, although no corrections to other parameters are applied.
11. Therefore you should enter 1 as the number of rotors for this molecule and then press enter.
12. You will now be prompted to enter the group ID's for each group in ethane, and their respective quantities in the format "GROUP ID, QUANTITY".
13. The "GROUP IDs" and their contributions are stored in a series of files entitled HC, CDOT, CLC, CYCH, HCN, HCO, INT. These files contain the above information for hydrocarbons, radicals, halogens, cyclic species,

nitrogen containing compounds, oxygenates and steric + other corrections respectively.

- The files themselves contain the GROUP ID followed by the relevant contributions of that group to the thermochemical parameters.

UNITS:KCAL

84	Hf	S	Cp: 300	400	500	600	800	1000	1500
C/C/H3,	-10.04	30.30	6.23	7.92	9.44	10.79	13.04	14.78	17.61
C/CB/H3,	-10.04	30.41	6.19	7.84	9.40	10.79	13.02	14.77	17.58
C/CD/H3,	-10.04	30.41	6.19	7.84	9.40	10.79	13.02	14.77	17.58
C/CT/H3,	-10.04	30.41	6.19	7.84	9.40	10.79	13.02	14.77	17.58
C/C2/H2,	-4.98	9.42	5.45	6.80	8.25	9.35	11.07	12.34	14.20
C/C3/H,	-1.95	-12.07	4.54	6.00	7.17	8.05	9.31	10.05	11.18
C/C4,	0.02	-35.10	4.13	5.63	6.93	8.14	10.24	12.08	15.56
CD/H2,	6.27	27.61	5.10	6.36	7.51	8.50	10.07	11.27	13.19
CD/C/H,	8.64	7.97	4.16	5.03	5.81	6.50	7.65	8.45	9.62
CD/C2,	9.60	-12.70	4.10	4.61	4.99	5.26	5.80	6.08	6.36
CD/CD/H,	6.78	6.38	4.46	5.79	6.75	7.42	8.35	9.11	10.09

GROUP IDs or BDE Groups Contribution of group to heat of formation at 298.15 K, entropy at 298.15 K and heat capacities over a range of temperatures

- Again, ethane contains only two identical groups, so enter "C/C/H3 2" into the THERM interface and hit enter.
- You are now asked to enter the symmetry number of your molecule. This symmetry number should incorporate symmetry contributions from both internal and external rotations of the molecule. The two methyl groups in ethane both have an internal symmetry number of 3 (rotation of the CH3 group through 120 degrees leads to an indistinguishable structure,  $360/120 = 3$  so  $\sigma = 3$ ). As there are two methyl groups the symmetry number from internal rotation is  $3 \times 3 = 9$ . Ethane also has an external plane of symmetry whereby if the whole molecule is rotated through 180 degrees, the structure formed is indistinguishable from the original one, this giving an external symmetry number of  $360/180 = 2$ . The total symmetry number of ethane, and all linear alkanes, is therefore  $3 \times 3 \times 2 = 18$ . Type this in and press enter.

```

C:\DOCUME~1\kieren\Desktop\therm\THERM.EXE
605 groups in the database
You must enter a total of 1 different groups
<enter " D " to re-enter the last group>
<enter " Q " to start a new species>
<enter " L " to list group database>

ENTER: "GROUP ID,QUANTITY"
ENTER GROUP # 1
C/C/H3 2
Enter symmetry # for molecule
18
  
```

17. You should now be presented with a screen showing the computed thermochemistry of ethane:

```

C:\DOCUME~1\kieren\Desktop\therm\THERM.EXE
Thermo estimation for molecule
C2H6                                     C2H6

Gr # - GROUP ID - Quantity
  1 - C/C/H3 - 2

UNITS: Hf<Kcal/mol>  S & Cp {cal/mol K}
      Hf  S    Cp 300  400  500  600  800  1000  1500
      -20.08  54.86  12.46  15.84  18.88  21.58  26.08  29.56  35.22
      CPINF  42.72
Symmetry number used to correct S value is      18
EDIT THESE RESULTS?      "Y" OR <"N">
  
```

18. If you consult the NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry/>), you can see that the computed heat of formation of  $-20.08 \text{ kcal mol}^{-1}$  is in excellent agreement with recommended values of ranging from  $-20.00 - -20.24 \text{ kcal mol}^{-1}$ , likewise the computed heat capacities are in good agreement with recommended data.
19. Type N into the THERM window when asked if you would like to edit these results and hit enter.
20. You will be presented with the following options in the 'SPECIES ESTIMATION OPTIONS MENU':

```

C:\DOCUME~1\kieren\Desktop\therm\THERM.EXE
          SPECIES ESTIMATION OPTIONS MENU
Units:  Kcal/mol < cal/mol K >

-----
R      -  CALCULATE RADICAL BASED UPON PREVIOUS SPECIES
F      -  ADD CURRENT SPECIES TO OUTPUT FILE
H      -  TOGGLE <SHORT/LONG> MENU
P      -  RETURN TO PREVIOUS SPECIES SCREEN
RETURN -  ENTER A NEW SPECIES
L      -  LIST GROUPS
Q      -  RETURN TO MAIN MENU <choose "F"
          first; current species is discarded
          when you return to MAIN menu>
X      -  EXIT PROGRAM
S      -  GET SPECIES FROM < *.DOC > FILE
?      -  HELP
U      -  CHANGE CURRENT UNITS TO : KJ/mol <J/mol K>

enter option : < ENTER NEW SPECIES >
  
```

21. Type F and hit enter so that we can store this calculation in a file. When asked to provide an output filename, type C2H6 and press enter. Enter the remaining options as follows:

```

C:\DOCUME~1\kieren\Desktop\therm\THERM.EXE
Enter output filename:
< no file extension is needed >:
C2H6

CREATE DOCUMENT FILE [ Y or N ]
enter choice: < Y >
Y
choose output units for LST file
1- Kcal/mol <cal/mol K> 2- KJ/mol <J/mol K >
enter option < 1 >
1

enter title for *.LST file output < blank or Q= no title >
C2H6

```

22. You will now be returned to the 'SPECIES ESTIMATION OPTIONS MENU'.
23. Press R and hit enter in order estimate thermochemistry of the ethyl radical (C2H5).
24. You will now be presented with a screen showing a list of Bond Increment names:

```

C:\DOCUME~1\kieren\Desktop\therm\THERM.EXE

177 - P          178 - IC4H9      179 - C2H5
180 - NEOC5     181 - S          182 - CC.C
183 - RCCJC     184 - RCGJCC    185 - T
186 - UIN       187 - UINS       188 - ALLYLP
189 - ALLYLS    190 - ALLYLT    191 - C#CJ
192 - C#CCJ     193 - C#CCJC    194 - C#CCJC2
195 - C*C*CJ    196 - C*CJC*C  197 - LC*CJC*C
198 - L2C*CJC*C 199 - C*CCJC*C 200 - C*CC*CCJ
201 - CJC*CC#C  202 - CYC3      203 - CYC4
204 - CYC4E     205 - CYPD      206 - CYPENE
207 - CYC5H9    208 - CYCJCH3  209 - CHD
210 - CHD14     211 - CHENE     212 - CHENEA
213 - CYC7H7    214 - PH1       215 - NAPH1
216 - NAPH2     217 - BENZYLP   218 - BENZYLS
219 - BENZYL    220 - CH3O      221 - ROCOJ
222 - ALKOXY    223 - UINOXY    224 - C*CHOJ
225 - C*CCDOJ   226 - PHENOXY   227 - C*CC*COJ
228 - CJOH      229 - CJOR      230 - CJOCQ
231 - CCJOH     232 - CCJOC     233 - RCJOC

ENTER BOND INCREMENT NAME ONLY
enter option : < Q >

```

25. These names correspond to the various types of C-H bonds which may be present in a wide range of homologous series of compounds. These GROUP IDs and corresponding Bond Increment values are stored in a file called BD in the folder you have been given. We will refer to these Bond Increment values as BDE Groups later in this manual.
26. The file contains data on the heat of reaction for the reaction:



27. As the thermochemistry of your stable compound is known (as we have just estimated it) and the thermochemistry of H is well known. We can imply thermochemistry for the radical based on the type of C–H bond being broken, and the corresponding heat of reaction, entropy of reaction and heat capacity of reaction as below:

94 -	del H rxn	S	Cp:300	400	500	600	800	1000	1500
P,	101.10	2.61	-0.77	-1.36	-1.91	-2.40	-3.16	-3.74	-4.66
IC4H9	101.10	2.11	-0.77	-1.36	-1.91	-2.40	-3.16	-3.74	-4.66
C2H5	101.10	2.04	-0.35	-1.25	-1.80	-2.23	-3.15	-3.78	-5.06
NEOC5	101.10	3.03	-0.59	-1.32	-2.05	-2.65	-3.50	-4.06	-4.87
S,	98.45	4.44	-1.50	-2.33	-3.10	-3.39	-3.75	-4.45	-5.20
CC.C	98.45	4.51	-1.30	-2.36	-3.02	-3.44	-3.98	-4.36	-4.99
RCCJC	98.45	5.13	-1.54	-2.77	-3.49	-3.90	-4.35	-4.64	-5.14
RCCJCC	98.45	4.90	-1.71	-3.14	-3.92	-4.33	-4.71	-4.92	-5.29
T,	96.50	5.24	-0.78	-2.48	-3.55	-4.15	-4.75	-5.02	-5.39
VIN,	111.20	1.39	-0.19	-0.75	-1.36	-1.92	-2.82	-3.49	-4.53
VINS,	109.00	1.81	-0.34	-1.21	-1.94	-2.52	-3.34	-3.91	-4.76

Bond Increment Name Heat of Reaction, Entropy of Reaction and change in heat capacity for reaction

28. In this case, the reaction  $C_2H_6 \rightarrow C_2H_5 + H$  is breaking a primary C-H bond, which is denoted as C2H5 in the BD file.
29. Enter C2H5 into the Bond Increment screen of THERM and press enter.
30. The symmetry number of the ethyl radical = 6 so enter the following fields like so:

```

C:\DOCUMENTS\kieren\Desktop\therm\THERM.EXE
PARENT = C2H6
C2H6
enter the symmetry number for the radical
6
Enter radical name<ID>
C2H5
  
```

31. Enter the molecular formula when prompted.
32. Enter the number of rotors for the molecule (1)
33. You should now be presented with a screen as seen overleaf detailing the thermochemical parameters, the symmetry number used to correct the entropy of C2H5 and the correction to the entropy for the unpaired radical in the molecule.
34. Press N and hit enter as no alterations to the thermochemistry are necessary.
35. You will be returned to the 'SPECIES ESTIMATION OPTIONS MENU'.
36. Press F and hit enter to add this species to the output files.

```

C:\DOCUME~1\kieren\Desktop\therm\THERM.EXE
Thermo estimation for radical
C2H5
RADICAL BASED UPON PARENT C2H6 C2H5
PARENT SYMMETRY 18
Gr # - GROUP ID - Quantity
1 - C/C/H3 - 2
2 - C2H5 - 1
UNITS: Hf<Kcal/mol> S & Cp <cal/mol K>
Hf S Cp 300 400 500 600 800 1000 1500
28.92 59.08 12.11 14.59 17.08 19.35 22.93 25.78 30.16
CPINF 36.76
Symmetry number used to correct S value is 6
R ln(2) has been added to S to account for unpaired electron
bond dissociation energy used = 101.10
EDIT THESE RESULTS? "Y" OR <"N">

```

37. If you look in your working directory, you should now have two files named C2H6.LST and C2H6.DOC. These files contain (respectively) a list of computed thermochemical data, and the GROUP IDs used to compute the thermochemical data itself. The \*.LST file will appear as follows if you open it in a text editor:

```

C2H6
SPECIES      Hf      S      Cp 300      400      500      600      800      1000      1500
C2H6      -20.08    54.86    12.46    15.84    18.88    21.58    26.08    29.56    35.22
C2H5      28.92    59.08    12.11    14.59    17.08    19.35    22.93    25.78    30.16

```

38. Press Q and hit enter to return the main THERM menu.
39. Now we will create a NASA Format Polynomial for C2H6 and C2H5, which can be used as input for kinetic modelling codes (Chemkin, Cantera, OpenSmoke etc.)
40. Press 8 and hit enter in order to run the 'THERMFIT' module of THERM.

```

C:\DOCUME~1\kieren\Desktop\therm\THERM.EXE
THERM MAIN MENU
Units: Kcal/mol < cal/mol K > 8/15/13

1 - ENTER/ESTIMATE SPECIES      5 - REVIEW <LST FORMAT FILE>
2 - VIEW GROUPS                6 - GET SPECIES FROM FILE {*.DOC}
3 - SELECT SHORT MENU          7 - ReWrite THERMO FILES {*.DOC, *.LST}
4 - SELECT LIST FILE {*.LST}   8 - RUN THERMFIT create NASA {*.DAT}
    9 - RUN THERMRXN <calculate dU, dH, dS, dG for reaction>
    10 - Sort & ReWrite THERMO FILES < *.DOC, *.LST >
    11 - Sort/Write "LST" file <or Write w/ new Units >
        < no "DOC" format file is needed >
    12 - RUN THERMLST <LIST NASA FORMAT FILE> /create *.LST
    13 - DOS utilities
    U - CHANGE CURRENT UNITS TO : KJ/mol <J/mol K>
        * - CLOSE ALL OPENED FILES
        X - EXIT PROGRAM
        ? - HELP

enter option : < 1 >

```

41. You will be prompted to enter the .LST file name used as input for fitting. Enter C2H6 and press enter.
42. When asked to enter the name of the output filename, type C2H6 and press enter.
43. The C2H6.DAT file will be created and should now be visible in your folder (C2H6.DAT). Open it in a text editor and it should appear as follows. These polynomials can be copied and pasted directly into simulation codes if desired.

```

THERMO
  300.000  1500.000  5000.000
C2H6      8/14/13 THERMC  2H  6  0  OG  300.000  5000.000 1383.000  11
  6.05972630E+00 1.30382837E-02-4.48103942E-06 6.97762095E-10-4.05606353E-14  2
-1.35751226E+04-1.28608001E+01 4.78623203E-02 2.40569127E-02-1.15155912E-05  3
  2.48666238E-09-1.78343944E-13-1.10923014E+04 2.06544071E+01  4
C2H5      8/15/13 THERMC  2H  5  0  OG  300.000  5000.000 1387.000  11
  5.88784390E+00 1.03076793E-02-3.46844396E-06 5.32499257E-10-3.06512651E-14  2
  1.15065499E+04-8.49651771E+00 1.32730217E+00 1.76656753E-02-6.14926558E-06  3
-3.01143466E-10 4.38617775E-13 1.34284028E+04 1.71789216E+01  4
END

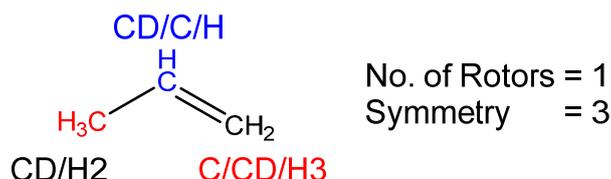
```

44. Polynomials can also be turned into .LST files using the THERM package.
45. You should now be on the THERM main menu, press 12 and hit enter to access the 'THERMLST' module of THERM.
46. When prompted, enter C2H6 as the input file name
47. Enter C2H6\_TEST as the output file name.
48. Select kcal/mol as the unit.
49. Select the the SHORT format for the output table.
50. Enter a title line if you wish.
51. The C2H6\_TES.LST file should now be in your working directory, compare its contents with the original estimated thermochemical data. They should be slightly different from due to the fitting procedures used for the polynomial.

## Propene and Allylic and Vinyl Radicals

Now we will estimate thermochemistry for the propene molecule and its three radicals. The molecular structure, groups, no. of rotors and symmetry of propene are presented below.

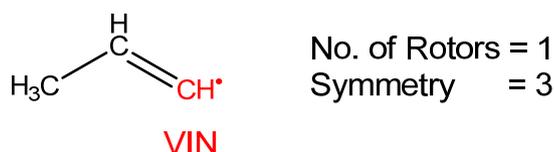
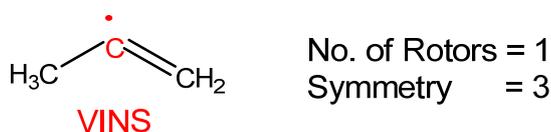
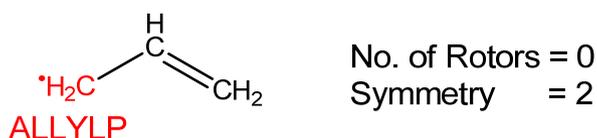
Use THERM to create thermochemistry, a .LST file and a NASA format polynomial for C<sub>3</sub>H<sub>6</sub> following the instructions described previously.



The thermochemistry for this species should appear as below, compares this data the NIST Chemistry Webbook, and/or the Burcat Database (<http://garfield.chem.elte.hu/Burcat/BURCAT.THR>)

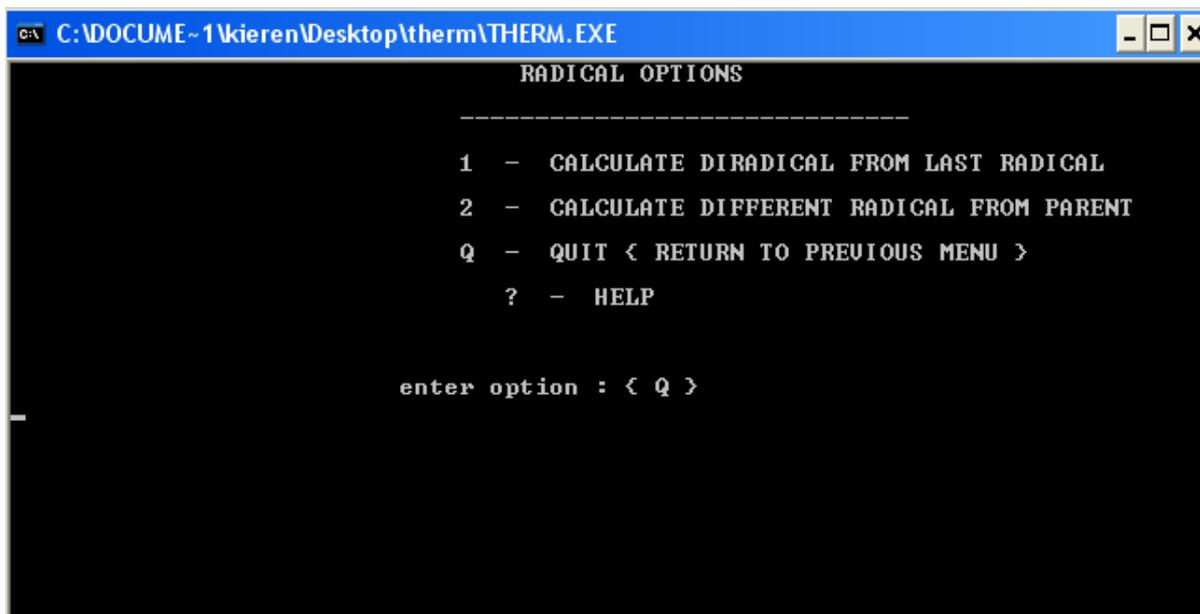
SPECIES	Hf	S	Cp	300	400	500	600	800	1000	1500
C <sub>3</sub> H <sub>6</sub>	4.87	63.81	15.45	19.23	22.72	25.79	30.74	34.49	40.39	

Once the parent species has been estimated, we can now proceed to estimating thermochemistry for the three propene radicals below. The bond increment names, no. of rotors and symmetry numbers of all three radicals are as follow:



Again, follow the instructions outlined in the first section of this manual (being sure to add each species to the output file as you create them). When you have estimated thermochemistry for the ALLYLP radical above, you will be presented with the screen below when you attempt to estimate

thermochemistry for the subsequent two radicals. In both cases select option 2 – ‘CALCULATE DIFFERENT RADICAL FROM PARENT’.

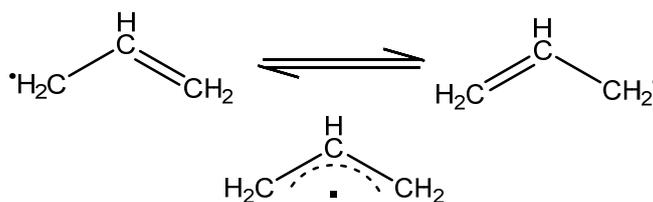


When you have estimated thermochemistry for all four species and added them to a .LST file, press Q to return to the main menu and create a .DAT file containing NASA polynomials.

The .LST file should appear as follows:

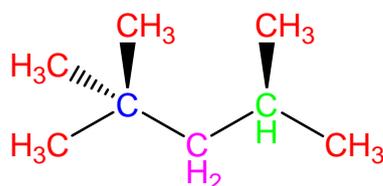
SPECIES	Hf	S	Cp	300	400	500	600	800	1000	1500
C3H6	4.87	63.81	15.45	19.23	22.72	25.79	30.74	34.49	40.39	
ALLYLP	40.97	62.05	14.83	18.67	21.94	24.67	28.90	32.03	36.90	
VINS	61.77	65.62	15.11	18.02	20.78	23.27	27.40	30.58	35.63	
VIN	63.97	65.20	15.26	18.48	21.36	23.87	27.92	31.00	35.86	

Note the difference in the relative stability of the three radicals, the ALLYLP radical is  $\approx 20$  kcal mol<sup>-1</sup> more stable than the secondary vinylic radical, and  $\approx 23$  kcal mol<sup>-1</sup> more stable than the primary vinylic radical. This relative stability stems from the ability of the ALLYLP radical to delocalize its unpaired electron create a hybrid resonance structure as seen below. The primary and secondary vinylic radicals cannot resonate in this fashion and as a result are much more unstable.



## Iso-octane (2,2,4-Trimethylpentane)

The chemical structure, no. of rotors, symmetry number and relevant groups and their number are provided below for iso-octane (C<sub>8</sub>H<sub>18</sub>). Use THERM to estimate thermochemistry for this species, and generate .LST and .DAT files.



No. of Rotors = 7  
Symmetry = 729

GROUPS:

C/C/H3 5

C/C4 1

C/C2/H2 1

C/C3/H 1

GAUCHE 3

H/REPEL/15 1

The final thermochemical parameters will appear as follows:

SPECIES	Hf	S	Cp 300	400	500	600	800	1000	1500
ISOCTANE	-53.21	100.65	45.27	58.03	69.55	79.49	95.82	108.37	128.99

The NIST Chemistry Webbook recommends a heat of formation of iso-octane of  $-53.57 \text{ kcal mol}^{-1}$  – in excellent agreement with this estimation. Likewise, a recommendation of  $45.28 \text{ cal mol}^{-1} \text{ K}^{-1}$  is provided for the heat capacity of the gas at 300 K, in excellent agreement with the group additivity prediction.

If you analyse the INT file, and search for the GAUCHE correction, you will see that each GAUCHE correction increases the computed heat of formation by  $0.8 \text{ kcal mol}^{-1}$ , in this case there are three GAUCHE corrections which increases the heat of formation predicted by the group contributions by  $2.4 \text{ kcal mol}^{-1}$ . Likewise, the 1,5 H interaction (H/REPEL/15) increases the predicted heat of formation by  $1.5 \text{ kcal mol}^{-1}$ . The GAUCHE and H/REPEL/15 corrections therefore increase the predicting heat of formation of iso-octane by  $3.9 \text{ kcal mol}^{-1}$ . These corrections are therefore non-negligible and one must be prudent when estimating thermochemistry for branched alkanes as a result. One should also keep in mind that when using THERM to estimate thermochemistry for radical species, one must estimate the parent from which it is formed first. Therefore, if these corrections are overlooked, errors can propagate into the thermochemistry for not only the stable species, but also any radical species which is derived from it. This can in turn perturb computed kinetic parameters for reactions in kinetic mechanisms due to perturbations, or errors even, in the equilibrium constants between reactants and products.

Iso-octane also has an extremely high symmetry number of 729. A symmetry number of 243 ( $3^5$ ) arises from the internal rotation of the 5 methyl groups highlighted in red above, and a further three fold symmetry number arises from rotation of the tertiary-butyl group about the C-CH<sub>2</sub> axis in the molecule, therefore increasing this number to  $3^6$ . The symmetry of the molecule is therefore corrected by  $-R \cdot \ln(729) = -13.09 \text{ cal mol}^{-1} \text{ K}^{-1}$ , again a non-negligible adjustment to the thermochemistry of this species. Again, given that the forward and reverse kinetic parameters are linked via the Gibbs Free Energy of reaction, errors in the predicted entropy of an individual species, can perturb the reactive flux in a chemical kinetic simulation due to errors in the equilibrium constants.

## Dimethyl Ether and its Intermediates

Overleaf we see a schematic representation of the primary oxidation reactions of dimethyl ether. The dimethyl ether radical ( $\text{CH}_3\text{O}\dot{\text{C}}\text{H}_2$ ) can initially be formed from unimolecular decomposition of the fuel via C–H fission, or once a radical pool has developed, abstraction of a hydrogen atom from the alkyl site of the fuel can occur.

At high temperatures, this radical can be consumed (exclusively) via  $\beta$ -scission to produce formaldehyde ( $\text{CH}_2\text{O}$ ) and methyl radical ( $\dot{\text{C}}\text{H}_3$ ). However, at lower temperatures where there is insufficient thermal energy to break the C–O bond of this radical, molecular oxygen ( $\text{O}_2$ ) can recombine with the  $\text{CH}_3\text{O}\dot{\text{C}}\text{H}_2$  radical forming the  $\text{CH}_3\text{OCH}_2\text{O}\dot{\text{O}}$  radical. This radical can isomerize forming the  $\dot{\text{C}}\text{H}_2\text{OCH}_2\text{OOH}$  radical which in turn can either decompose to form  $\text{CH}_2\text{O}$  and  $\dot{\text{C}}\text{H}_2\text{OOH}$  radical, or it can undergo another addition reaction with  $\text{O}_2$  to form  $\dot{\text{O}}\text{OCH}_2\text{OCH}_2\text{OOH}$ .

$\dot{\text{O}}\text{OCH}_2\text{OCH}_2\text{OOH}$  in turn can isomerize to form  $\text{HOOCH}_2\text{O}\dot{\text{C}}\text{HOOH}$  which will subsequently decompose to form  $\text{HOOCH}_2\text{OCHO}$  and  $\dot{\text{O}}\text{H}$  radical.  $\text{HOOCH}_2\text{OCHO}$  will decompose readily via unimolecular homolytic fission to form  $\dot{\text{O}}\text{CH}_2\text{OCHO}$  radical and another  $\dot{\text{O}}\text{H}$  radical. These low temperature pathways result in the production of two reactive  $\dot{\text{O}}\text{H}$  radicals (chain branching) which can further react with the fuel and thus propagating the chain reaction ultimately leading to ignition.

It is the competition between the unimolecular decomposition of  $\text{CH}_3\text{O}\dot{\text{C}}\text{H}_2$  and the reaction of  $\text{CH}_3\text{O}\dot{\text{C}}\text{H}_2 + \text{O}_2$  forming  $\text{RO}_2$  species which creates the famous Negative Temperature Coefficient (NTC) ignition behaviour of straight-chain alkane fuels such as the Primary Reference Fuels (PRFs).

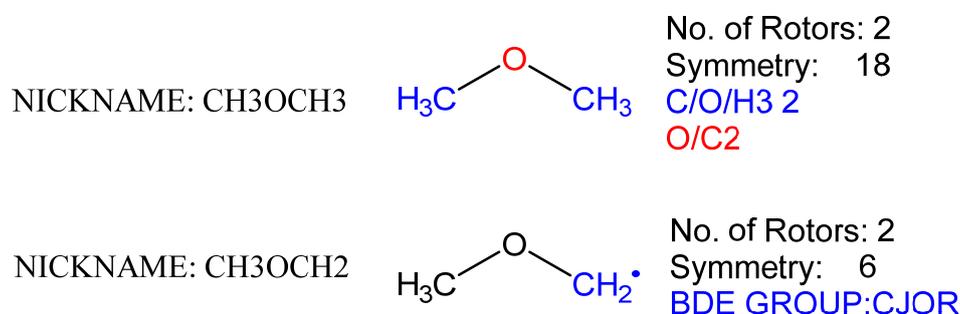
$\text{RO}_2$  and their derivatives are hugely important intermediates in the oxidation of many fuels therefore and estimating their thermodynamic properties is therefore of importance.

Here we will now estimate thermochemistry for dimethyl ether, its radical and some  $\text{RO}_2$  species formed during dimethyl ether oxidation.



The chemical structure, no. of rotors, symmetry number and relevant groups and their number are provided below for dimethyl ether. Use THERM to estimate thermochemistry for this species, and generate .LST and .DAT files.

When asked to define the name of the species in THERM, use the nickname assigned below. Note the nomenclature in the BDE group below, CJOR it has been common in the past to refer to radical sites in molecules as 'J' when carrying out simulations using the Chemkin 'NICKNAME' format for species. There is no chemical reason for the use of J to denote the radical sites. The 'R' below refers to any substituent group R which could be bonded to the oxygen of the chain.

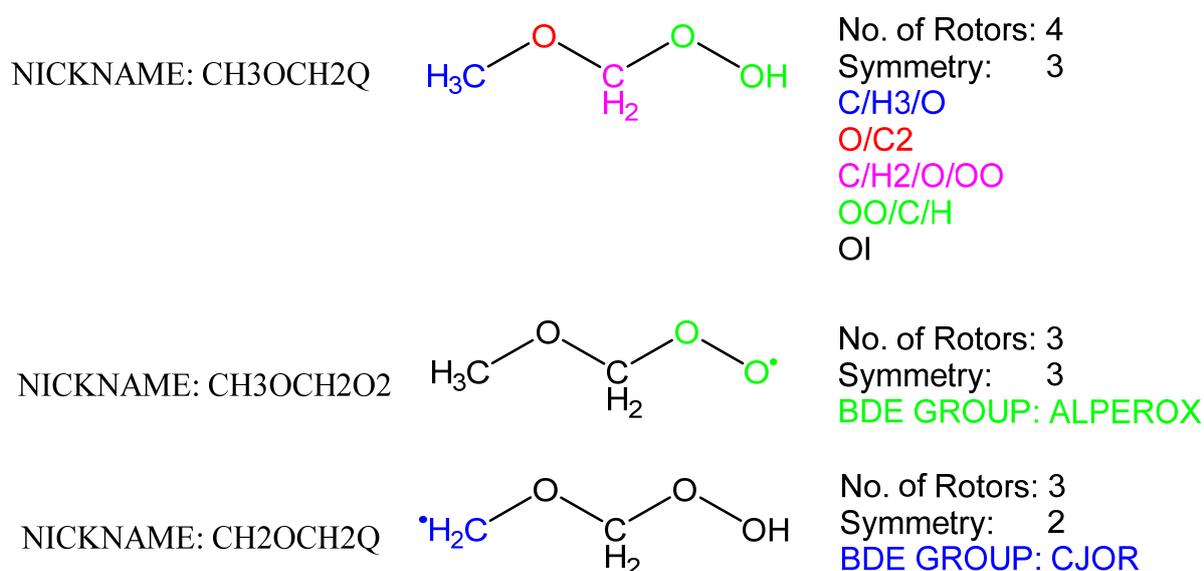


The computed thermochemistry should be as follows:

SPECIES	Hf	S	Cp	300	400	500	600	800	1000	1500
CH3OCH3	-44.00	63.74	15.59	18.64	21.77	24.67	29.59	33.40	39.40	
CH3OCH2	1.10	68.05	14.60	17.14	20.01	22.49	26.26	29.36	34.58	

In order to estimate thermochemistry for the product of O<sub>2</sub> addition to CH<sub>3</sub>OCH<sub>2</sub>, seen below as 'CH<sub>3</sub>OCH<sub>2</sub>O<sub>2</sub>', we must first estimate thermochemistry for its parent species referred to below as CH<sub>3</sub>OCH<sub>2</sub>Q below, but chemically known as hydroperoxy(methoxy)methane. The use of the letter Q has been historically used to indicate the presence of a hydroperoxy group in a molecule, although again, there is no chemical meaning to this definition, it is merely convenient shorthand.

Also note the OI group present in the molecule. OI denotes an 'Optical Isomer' group. Optical isomerism is a form of isomerism whereby non-superimposable mirror images of a molecule can be drawn, thus leading to two distinct representations of the structure. The addition of the -OOH moiety to the molecule in this case leads to the presence of two optical isomers (which are accounted for by the inclusion of 1 OI group) for hydroperoxy(methoxy)methane. This leads to an increase in the entropy of hydroperoxy(methoxy)methane of  $+R \times \ln(2) = 1.37 \text{ cal mol}^{-1} \text{ K}^{-1}$ .



The computed thermochemistry should be as follows:

SPECIES	Hf	S	C <sub>p</sub> 300	400	500	600	800	1000	1500
CH <sub>3</sub> OCH <sub>2</sub> Q	-72.51	85.07	23.75	28.93	32.83	36.20	41.61	45.00	.00
CH <sub>3</sub> OCH <sub>2</sub> O <sub>2</sub>	-38.91	83.92	21.70	26.09	29.28	32.11	36.89	40.03	.00
CH <sub>2</sub> OCH <sub>2</sub> Q	-27.41	88.00	22.76	27.43	31.07	34.02	38.28	40.96	.00

Now that we know the thermochemistry for  $\text{CH}_3\text{O}\dot{\text{C}}\text{H}_2$  and  $\text{CH}_3\text{OCH}_2\text{O}\dot{\text{O}}$ , we can compute the thermochemistry for the reaction  $\text{CH}_3\text{O}\dot{\text{C}}\text{H}_2 + \text{O}_2 = \text{CH}_3\text{OCH}_2\text{O}\dot{\text{O}}$  as  $\text{O}_2$  is well known:

SPECIES	Hf (298)	S (298)	CP300	CP400	CP500	CP600	CP800	CP1000	CP1500
O2	.00	49.03	7.02	7.20	7.43	7.67	8.07	8.34	8.72

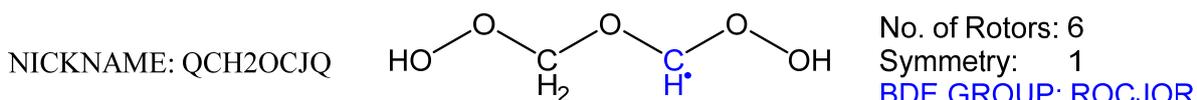
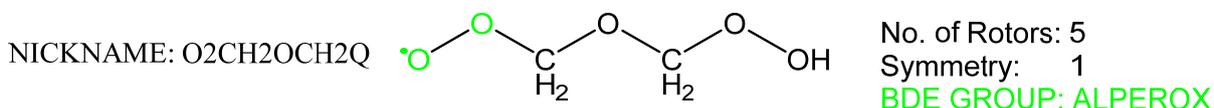
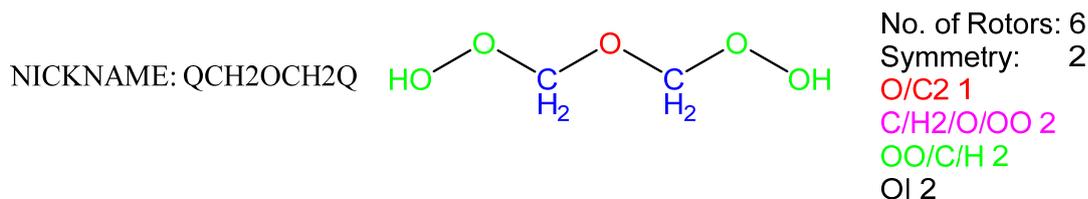
		Cp (cal/mol K)								
Species		Hf (kcal/mol)	S (cal/mol K)	300	400	500	600	800	1000	1500
Reactants	CH3OCH2	1.10	68.05	14.60	17.14	20.01	22.49	26.26	29.36	34.58
	O2	0.00	49.03	7.02	7.20	7.43	7.67	8.07	8.34	8.72
Products	CH3OCH2O2	-38.91	83.92	21.70	26.09	29.28	32.11	36.89	40.03	0.00
Products - Reactants =>		-40.01	-33.16	0.08	1.75	1.84	1.95	2.56	2.33	

The reaction is exothermic by  $-40.01 \text{ kcal mol}^{-1}$  at 298 K (a new bond is being formed which releases energy) but also proceeds with a loss in entropy ( $-33.16 \text{ cal mol}^{-1} \text{ K}^{-1}$  at 298 K) due to the formation of a single species from two others.

The  $\text{CH}_3\text{OCH}_2\text{O}\dot{\text{O}}$  radical can isomerize to  $\dot{\text{C}}\text{H}_2\text{OCH}_2\text{O}$  through an intramolecular hydrogen atom abstraction in an endothermic reaction ( $11.50 \text{ kcal mol}^{-1}$  at 298 K).

		Cp (cal/mol K)								
Species		Hf (kcal/mol)	S (cal/mol K)	300	400	500	600	800	1000	1500
Reactants	CH3OCH2O2	-38.91	83.92	21.70	26.09	29.28	32.11	36.89	40.03	0.00
Products	CH2OCH2O	-27.41	88.00	22.76	27.43	31.07	34.02	38.28	40.96	0.00
Products - Reactants =>		11.50	4.08	1.06	1.34	1.79	1.91	1.39	0.93	

The  $\dot{\text{C}}\text{H}_2\text{OCH}_2\text{O}$  radical can either decompose to produce  $\text{CH}_2\text{O} + \dot{\text{C}}\text{H}_2\text{OOH}$  or  $\text{O}_2$  can again add to this radical forming  $\dot{\text{O}}_2\text{CH}_2\text{OCH}_2\text{O}$  whose thermochemistry we can also estimate as shown overleaf.



The computed thermochemistry should be as follows (the 'Q' at the end of the second species may be missing as THERM has a limit of 9 on the number of characters in the species name):

SPECIES	HF (298)	S (298)	CP300	CP400	CP500	CP600	CP800	CP1000	CP1500
QCH2OCH2Q	-101.02	103.64	31.91	39.22	43.89	47.73	53.63	56.60	.00
O2CH2OCH2Q	-67.42	103.87	29.86	36.38	40.34	43.64	48.91	51.63	.00
QCH2OCJQ	-57.12	106.17	31.78	38.55	42.58	45.84	50.81	53.11	.00

Again, now that we know the thermochemistry for  $\dot{\text{C}}\text{H}_2\text{OCH}_2\text{Q}$  and  $\dot{\text{O}}_2\text{CH}_2\text{OCH}_2\text{Q}$ , we can compute the thermochemistry for the reaction  $\dot{\text{C}}\text{H}_2\text{OCH}_2\text{Q} + \text{O}_2 = \dot{\text{O}}_2\text{CH}_2\text{OCH}_2\text{Q}$ .

		Cp (cal/mol K)								
Species		Hf (kcal/mol)	S (cal/mol K)	300	400	500	600	800	1000	1500
Reactants	CH2OCH2Q	-27.41	88.00	22.76	27.43	31.07	34.02	38.28	40.96	0.00
	O2	0.00	49.03	7.02	7.20	7.43	7.67	8.07	8.34	8.72
Products	O2CH2OCH2Q	-67.42	103.87	29.86	36.38	40.34	43.64	48.91	51.63	0.00
Products - Reactants =>		-40.01	-33.16	0.08	1.75	1.84	1.95	2.56	2.33	

Compare this reaction enthalpy, entropy and heat capacity change with that computed previously for the first O<sub>2</sub> addition reaction. The two are effectively identical and the consistency which a group additivity approach to thermochemistry provides is highlighted in this instance.

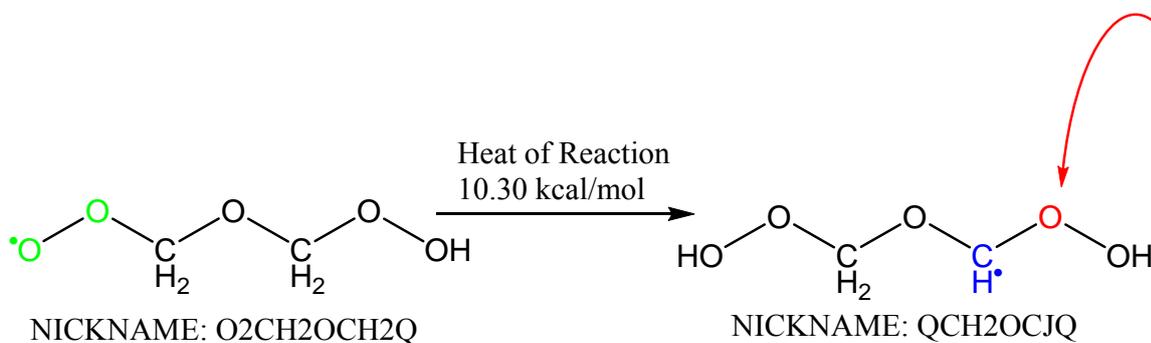
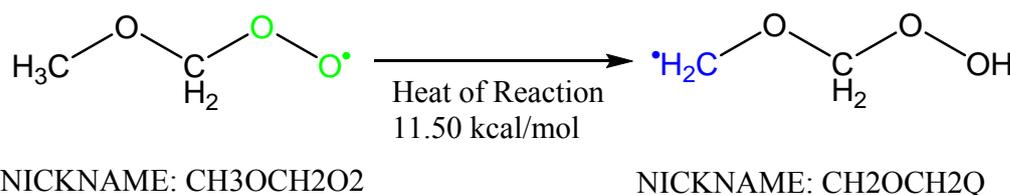
Likewise the isomerization reaction  $\dot{\text{O}}_2\text{CH}_2\text{OCH}_2\text{Q} = \text{QCH}_2\text{O}\dot{\text{C}}\text{H}\text{Q}$  shows the following thermodynamic change:

				Cp (cal/mol K)						
	Species	Hf (kcal/mol)	S (cal/mol K)	300	400	500	600	800	1000	1500
Reactants	O2CH2OCH2Q	-67.42	103.87	29.86	36.38	40.34	43.64	48.91	51.63	0.00
Products	QCH2OCJQ	-57.12	106.17	31.78	38.55	42.58	45.84	50.81	53.11	0.00
Products - Reactants =>		10.30	2.30	1.92	2.17	2.24	2.20	1.90	1.48	

These are very similar to those seen before but NOT identical:

				Cp (cal/mol K)						
	Species	Hf (kcal/mol)	S (cal/mol K)	300	400	500	600	800	1000	1500
Reactants	CH3OCH2O2	-38.91	83.92	21.70	26.09	29.28	32.11	36.89	40.03	0.00
Products	CH2OCH2Q	-27.41	88.00	22.76	27.43	31.07	34.02	38.28	40.96	0.00
Products - Reactants =>		11.50	4.08	1.06	1.34	1.79	1.91	1.39	0.93	

In this respect group additivity allows us to account for small variations in chemical structure within a homologous series of species thus leading to reasonably refined estimations of thermochemical data. This consistency combined with flexibility makes it a robust and efficient tool for kinetic modelling of small and large chemicals.



Electronegativity of oxygen adjacent to the radical site weakens C-H bond thus making radical more stable. This is reflected in the heat of reaction of the second isomerization being 1.20 kcal/mol lower than that of the first one where this O group is absent.