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<th>Critical evaluation of thermochemical properties of C-1-C-4 species: updated group-contributions to estimate thermochemical properties</th>
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<td>Burke, S. M.; Simmie, J. M.; Curran, Henry J.</td>
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Critical evaluation of thermochemical properties of C₁–C₄ species; updated group-contributions to estimate thermochemical properties.

S. M. Burke, J. M. Simmie, and H. J. Curran

Combustion Chemistry Centre, National University of Ireland, Galway, Ireland

(Dated: 26 September 2014)

A review of literature enthalpies of formation and molar entropies for alkanes, alkenes, alcohols, hydroperoxides, and their associated radicals has been compiled and critically evaluated. By comparing literature values the overall uncertainty in thermochemical properties of small hydrocarbons and oxygenated hydrocarbons can be highlighted. In general there is good agreement between heat of formation values in the literature for stable species, however there is greater uncertainty in the values for radical species and for molar entropy values. Updated values for a group-additivity method for the estimation of thermochemical properties based on the evaluated literature data are proposed. The new values can be used to estimate thermochemical data for larger, combustion-relevant, species for which no calculations or measurements currently exist, with increased confidence.

Keywords: enthalpy of formation; molar entropy; specific heat capacity at constant pressure; group additivity; hydrocarbons; oxygenated hydrocarbons; combustion

I. INTRODUCTION

In order to describe the combustion of fuels, detailed chemical kinetic models require accurate thermodynamic and kinetic data. In general, chemical kinetic mechanisms define rate constants in a single direction only. Thermodynamic properties are used in the calculation of reverse rate constants, equilibrium constants, and the amount of heat released from a reaction. Therefore reliable values for thermodynamic properties are important in order to accurately predict rates of chemical reactions. Specific thermodynamic properties are required as input when carrying out modelling of combustion systems. Properties such as enthalpy of formation, \( \Delta_f H^\circ(298.15 \, \text{K}) \) and entropy, \( \Delta S^\circ \) functions, and heat capacities at constant pressure, \( C_p \) are included in mechanisms. Accurate heats of formation of smaller species are also important when using isodesmic reactions to determine the heat of formation of a given species.

A. Source of thermodynamic properties

A significant amount of data for thermodynamic properties exists in the literature. Much of this data is collated in the NIST database,\(^1\) Active Thermochi-

cal Tables (ATcT),\(^2\) Third Millennium Thermodynamic Database\(^3\) and from numerous experimental and theoretical studies. A recent \( ab \, \text{initio} \) study by Goldsmith \et al.\(^4\) reported thermochemical properties for over 200 combustion relevant species. A study by Verevkin \et al.\(^5\) collected and critically evaluated experimental data for enthalpies of formation in the liquid phase, enthalpies of vaporization, and enthalpies of formation in the gas phase for stable alkanes, alkenes, alkynes, alkylbenzenes, alkanols, ethers, ketones and aldehydes, carboxylic acids, esters, and carbonates.

Many of the thermodynamic properties recommended in the literature are derived from high-level \( ab \, \text{initio} \) calculations or state of the art experimental measurements and when considered independently appear to be of very high quality. However when these values are compared there can often be discrepancies. It is only when many literature values are compared that we get an idea of what the true uncertainty is for a thermodynamic property. It is noteworthy that while there are many studies in the literature that recommend or review values for the heat of formation of various stable species there are fewer that give molar entropies and heat capacities the same attention, and therefore these properties are less well known.

There are species relevant to the combustion community for which there are no published thermochemical data. For these cases the group additivity (GA) method developed by Benson,\(^6\) can be used to estimate thermochemical data. Each ‘heavy’ (non-hydrogen) atom in a molecule and its bonded atoms (known as a group) have specific thermodynamic properties which contributes to the enthalpy, entropy, and heat capacities of the molecule as a whole. The contributions of all groups are added and the molecule’s symmetry and number of rotors are accounted for. Benson’s GA method allows for the inclusion of corrections for interactions between non-bonded and large range interactions as found in larger molecules including: cis-trans interactions, gauche interactions and 1,5 hydrogen repulsions as described by Benson.\(^6\) Optical isomer corrections can be applied to molecules such as alkyl hydroperoxides and other chiral molecules, this is also discussed by Benson.\(^6\)

The THERM\(^7\) computer programme employs the group additivity (GA) method developed by Benson\(^6\) and can be used to estimate, edit, or enter thermody-
namic property data for gas phase molecules and radicals. THERM can generate thermochemistry of a stable molecule in NASA polynomial format as used in combustion modelling software such as CHEMKIN.

An example of the groups used for a simple molecule is included in Fig. 1 which identifies each non-hydrogen atom, the symmetry and number of rotors in the ethanol molecule. The primary carbon atom is bonded to another carbon and to three hydrogen atoms, C/C/H3, the methylene carbon is described as C/C/H2/O and the hydroxyl group is described by the group O/C/H.

1. Ideology of this study

This study has two main aims; firstly to develop an accurate database of thermodynamic properties from the literature of smaller species and secondly to use the data compiled to update the groups used in the GA method employed in THERM. The majority of values for the groups included in the GA method employed in THERM originate from Benson who first published group values in 1976. Computational capability has increased since the Benson groups were published and more accurate thermodynamic data has become available from experimental measurements and high level ab initio calculations.

The ideology behind this work was to determine whether the GA method can produce thermodynamic data that reflects the most recent experimental measurements and theoretical calculations for smaller species. If so the current GA method can be applied to generate reasonable estimates of thermodynamic properties for higher molecular weight species where accurate high-level calculations are difficult to perform.

In this vein a thorough literature review was undertaken in order to develop an accurate database of thermodynamic properties of smaller species to optimise the groups used in the GA method. The predictive power of the GA method was tested against the literature or the calculated values. The group values were optimised and updated to reflect the calculated and measured data. This was done in a hierarchical and systematic way, starting with alkanes, then alkenes, followed by alcohols, aldehydes, ketones, hydroperoxides and alcohol hydroperoxide species.

2. Optimisation method

In order to improve the agreement between thermochemical data from the GA method and the literature thermochemical data, changes to the group values were made. Further explanation of group values and the naming scheme utilised in THERM is included in \textsuperscript{6,7}. The GA values for thermodynamic properties were optimised in a hierarchical manner in order to reach agreement with the literature values.

For each molecular class alkane, alkene, etc and for each property, enthalpy of formation, entropy and specific heat at constant pressure the following procedure was used:

1. The literature values, $x_i$, for each species were averaged, $\bar{x} = \frac{\sum x_i}{n}$. If $x_i - \bar{x} \geq 2\sigma x_i$ was rejected and a new average sought.

2. $\sum (\bar{x}_i - \Gamma_i)^2$ was minimised (Microsoft Excel’s solver add-in\textsuperscript{9}) by varying the property value from the existing group additivity values, $\Gamma_i$.

3. Group values were optimised for one class of molecules at a time. They were then used in the generation of updated groups for other classes of molecules. For example, when investigating alkenes only the groups specific to alkenes were altered, the applicable alkane groups were not modified.

A 2$\sigma$ uncertainty was chosen to quantify the expected accuracy of each property as discussed by Ruscic\textsuperscript{10}; in essence this means that the true value should lie inside the quoted error bounds at least 19 times out of 20.

II. LITERATURE REVIEW OF THERMODYNAMIC PROPERTIES OF C\textsubscript{1}–C\textsubscript{4} SPECIES

Included in this section is a literature review of values for the enthalpy of formation at 298.15 K (abbreviated in Table I and all subsequent Tables to $\Delta f H^\circ$) and standard molar entropy of alkanes, alkenes, alcohols, hydroperoxides and their related radicals (abbreviated in Table II and all subsequent relevant Tables to $\Delta S^\circ$). Note that the term \textit{GA} in the Tables refers to the thermochemical property from group additivity after optimisation. The groups used to calculate each stable and radical species are also included in Tables XCIV and XCV.

The sources of the specific values in the Tables have been abbreviated as follows:
Calorimetry: determination of a heat of formation from an experimental measurement of the heat of combustion

Kinetics: derivation of thermodynamic value from the study of the forward and reverse rate constants of a reaction

RRHO: rigid-rotor harmonic-oscillator, model used by Chao and co-workers.11,12

DMC: Diffusion Monte Carlo


QCISDT: RCCISD(T)/cc-PV8QZ//B3LYP/6-311++G(d,p) method

TPEPICO: threshold photoelectron-photoion coincidence spectroscopy

TN: thermochemical network approach as implemented by the Active Thermochemical Tables (ATcT)²

MEI: Monoenergetic Electron Impact

RRKM: Rice-Ramsberger-Kassel-Marcus analysis

HEAT: High-accuracy Extrapolated Ab initio Thermochemistry

PMS: Photoionization Mass Spectrometer

B3LYP: Density functional theory method

CCSD(T): coupled-cluster method

ccCA: correlation consistent composite approach

UPS: Ultraviolet Photoelectron Spectroscopy

SLIF: Saturated Laser-Induced Fluorescence

MP 2–4: 2nd to 4th order Möller-Plesset perturbation theory

PM3: Parameterized Model number 3

A. Alkanes and alkyl radicals

1. Ethane

\[ \text{H}_3\text{C} \longrightarrow \text{CH}_3 \]

The thermodynamic properties of ethane have been studied extensively4,11,13–22 as shown in Tables I and II. The average heat of formation for ethane is \(-20.16 \text{ kcal mol}^{-1}\) with a standard deviation of 0.35 \text{ kcal mol}^{-1}. One of the calculated values from Rayne and Forest19 differs from the average by 1.09 kcal mol\(^{-1}\) which is more than twice the standard deviation. When it excluded the new average is \(-20.08 \text{ kcal mol}^{-1}\). Optimisation of the groups results in an heat of formation of \(-20.02 \text{ kcal mol}^{-1}\).

The average molar entropy for ethane is 54.76 \text{ cal K}^{-1} \text{ mol}^{-1} with a standard deviation of 0.06 \text{ cal K}^{-1} \text{ mol}^{-1}. Cao and Back15’s recommendation is 0.14 \text{ cal K}^{-1} \text{ mol}^{-1} greater than the average, which is more than twice the standard deviation. When it is excluded the average becomes 54.74 cal K\(^{-1}\) mol\(^{-1}\). Optimisation of the groups results in value 54.84 cal K\(^{-1}\) mol\(^{-1}\) which is 0.10 cal K\(^{-1}\) mol\(^{-1}\) higher than the average.

<table>
<thead>
<tr>
<th>Literature</th>
<th>(\Delta, H^*)</th>
<th>Year</th>
<th>Source</th>
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<tr>
<td>Chao et al.11</td>
<td>-20.24</td>
<td>1973</td>
<td>Calc.²</td>
</tr>
<tr>
<td>Cao and Back15</td>
<td>-20.20</td>
<td>1984</td>
<td>Exp.¹</td>
</tr>
<tr>
<td>Manion16</td>
<td>-20.00 ±0.10</td>
<td>1986</td>
<td>Rev.</td>
</tr>
<tr>
<td>Kollais et al.18</td>
<td>-20.10</td>
<td>2005</td>
<td>Calc.³</td>
</tr>
<tr>
<td>Baulch et al.17</td>
<td>-20.00</td>
<td>2005</td>
<td>Rev.</td>
</tr>
<tr>
<td>Rayne and Forest19</td>
<td>-19.81</td>
<td>2010</td>
<td>Calc.±</td>
</tr>
<tr>
<td>Rayne and Forest19</td>
<td>-21.18</td>
<td>2010</td>
<td>Calc.³</td>
</tr>
<tr>
<td>CRC²²</td>
<td>-20.08</td>
<td>1999</td>
<td>Rev.</td>
</tr>
<tr>
<td>3rd Millennium³</td>
<td>-20.04</td>
<td>2012</td>
<td></td>
</tr>
<tr>
<td>Goldsmith et al.⁴</td>
<td>-20.00 ±0.10</td>
<td>2012</td>
<td>Calc.⁵</td>
</tr>
<tr>
<td>Verevkin et al.⁵</td>
<td>-20.08</td>
<td>2013</td>
<td>Rev.</td>
</tr>
<tr>
<td>Standard Deviation</td>
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</table>

Recommen|dation | -20.08 | | |

| GA | 54.74 | | |

| RRHO | 54.84 | | |

| QCISDT | 54.97 | | |

| DMC | 54.74 | | |

| WIBD | 54.84 | | |

| * | CALORIMETRY | | |

| † | RRHO | | |

| ‡ | KINETICS | | |

| † | MD | | |

| § | WIBD | | |

| † | QCISDT | | |

TABLE I. Enthalpy of formation (kcal mol\(^{-1}\)) of ethane.

<table>
<thead>
<tr>
<th>Literature</th>
<th>S°</th>
<th>Year</th>
<th>Source</th>
</tr>
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<tr>
<td>Chao et al.11</td>
<td>54.76</td>
<td>1973</td>
<td>Calc.²</td>
</tr>
<tr>
<td>Cao and Back15</td>
<td>54.90</td>
<td>1984</td>
<td>Exp.²²</td>
</tr>
<tr>
<td>Lange’s Handbook²¹</td>
<td>54.76</td>
<td>1999</td>
<td>Rev.</td>
</tr>
<tr>
<td>Baulch et al.17</td>
<td>54.70</td>
<td>2005</td>
<td>Rev.</td>
</tr>
<tr>
<td>De Tar²⁰</td>
<td>54.73</td>
<td>2007</td>
<td>Rev.</td>
</tr>
<tr>
<td>CRC²²</td>
<td>54.78</td>
<td>1999</td>
<td>Rev.</td>
</tr>
<tr>
<td>3rd Millennium³</td>
<td>54.78</td>
<td>2012</td>
<td></td>
</tr>
<tr>
<td>Goldsmith et al.⁴</td>
<td>54.70 ±0.10</td>
<td>2012</td>
<td>Calc.†</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.06</td>
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</table>

Recommen|dation | 54.74 | | |

| G | 54.84 | | |

| RRHO | 54.74 | | |

| * | CALORIMETRY | | |

| † | RRHO | | |

| ‡ | KINETICS | | |

| † | MD | | |

| § | WIBD | | |

| † | QCISDT | | |

TABLE II. Molar entropy (cal K\(^{-1}\) mol\(^{-1}\)) of ethane.

2. Ethyl radical

\[ \text{H}_3\text{C} \longrightarrow \text{CH}_2 \]

The average of the literature heat of formation values for the ethyl radical is 28.26 kcal mol\(^{-1}\) with a standard deviation of 0.75 kcal mol\(^{-1}\). The recommendation from Kollais et al.18 differs from the average by 2.04 kcal mol\(^{-1}\) which is more than twice the standard deviation. Kollais et al.18 calculated the heats of formation of 22 molecules using the Quantum Monte Carlo (QMC) method. The
authors stated that the results using this method are less accurate than those using higher-levels of theory. When the Kollais et al.\textsuperscript{18} value is excluded the average becomes 28.65 kcal mol\textsuperscript{-1}. Optimisation of the groups results in an heat of formation of 28.65 kcal mol\textsuperscript{-1}. The average of the literature values for the molar entropy is 59.29 cal K\textsuperscript{-1} mol\textsuperscript{-1} with a standard deviation of 1.02 K\textsuperscript{-1} mol\textsuperscript{-1}. All values are within two standard deviations of the average.

### 3. Propane

Thermodynamic properties for propane has been the subject of several studies\textsuperscript{3,4,11,13,14,17,21,22,27} The values are included in Tables V and VI. The average of the literature heat of formation values for propane is $-24.94$ kcal mol\textsuperscript{-1} with a standard deviation of $0.12$ kcal mol\textsuperscript{-1}. The value from Goldsmith et al.\textsuperscript{4} differs from the average by $0.25$ kcal mol\textsuperscript{-1} which is more than twice the standard deviation. When it is excluded the average becomes $-24.92$ kcal mol\textsuperscript{-1}. Optimisation of the groups results in an heat of formation of $-25.02$ kcal mol\textsuperscript{-1}.

The average molar entropy is $64.83$ cal K\textsuperscript{-1} mol\textsuperscript{-1} with a standard deviation of $0.50$ cal K\textsuperscript{-1} mol\textsuperscript{-1}. Values that differ from the average by more than twice the deviation include the recommendation from Goldsmith et al.\textsuperscript{4} which is $1.30$ cal K\textsuperscript{-1} mol\textsuperscript{-1} larger than the average. Excluding this value results in an average of $64.63$ cal K\textsuperscript{-1} mol\textsuperscript{-1} which is $0.14$ cal K\textsuperscript{-1} mol\textsuperscript{-1} greater than the value estimated using group additivity after optimisation of 64.49 cal K\textsuperscript{-1} mol\textsuperscript{-1}.

### 4. n-Propyl radical

Table VII contains heat of formation values and Table VIII molar entropy values for the n-propyl radical. In general there is good agreement amongst both the $\Delta_fH^\circ$ (298.15 K) and $S^\circ$ (298.15 K) data that spans over
TABLE VII. Enthalpy of formation (kcal mol\(^{-1}\)) of \textit{n}\text{-}propyl radical.

<table>
<thead>
<tr>
<th>Literature</th>
<th>(\Delta_f H^\circ)</th>
<th>Year Source</th>
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<tbody>
<tr>
<td>Castelhano and Griller(^{26})</td>
<td>22.80</td>
<td>1982 Exp.</td>
</tr>
<tr>
<td>Holmes \textit{et al.}(^{29})</td>
<td>22.70</td>
<td>1988 Exp.**</td>
</tr>
<tr>
<td>Tsang(^{25})</td>
<td>23.95</td>
<td>1996 Rev.</td>
</tr>
<tr>
<td>Seetula and Slagle(^{30})</td>
<td>24.09 ±0.50</td>
<td>1997 Exp.*</td>
</tr>
<tr>
<td>Baulch \textit{et al.}(^{17})</td>
<td>24.00</td>
<td>2005 Rev.</td>
</tr>
<tr>
<td>Bodi \textit{et al.}(^{26})</td>
<td>24.21 ±0.24</td>
<td>2006 Exp.†</td>
</tr>
<tr>
<td>3\textsuperscript{rd}Millennium(^\dagger)</td>
<td>24.21</td>
<td>2012</td>
</tr>
<tr>
<td>Goldsmith \textit{et al.}(^{4})</td>
<td>24.30 ±0.90</td>
<td>2012 Calc.‡</td>
</tr>
<tr>
<td>Standard Deviation</td>
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<tr>
<td>Recommendation</td>
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<tr>
<td>\textit{GA}</td>
<td>24.03</td>
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</table>

\(^{1}\text{KINETICS}\) ** MEI  \(^{\dagger}\text{TPEPICO}\) \(\dagger\text{QCISDT}\)

TABLE VIII. Molar entropy (cal K\(^{-1}\) mol\(^{-1}\)) of \textit{n}\text{-}propyl radical.

<table>
<thead>
<tr>
<th>Literature</th>
<th>(S^\circ)</th>
<th>Year Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tsang(^{25})</td>
<td>69.17</td>
<td>1996 Rev.</td>
</tr>
<tr>
<td>Seetula and Slagle(^{30})</td>
<td>67.88 ±1.20</td>
<td>1997 Exp.*</td>
</tr>
<tr>
<td>Baulch \textit{et al.}(^{17})</td>
<td>69.20</td>
<td>2005 Rev.</td>
</tr>
<tr>
<td>3\textsuperscript{rd}Millennium(^\dagger)</td>
<td>69.34</td>
<td>2012 Calc.**</td>
</tr>
<tr>
<td>Goldsmith \textit{et al.}(^{4})</td>
<td>69.30 ±1.0</td>
<td>2012 Calc.**</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.72</td>
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<tr>
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<td>69.25</td>
<td></td>
</tr>
<tr>
<td>\textit{GA}</td>
<td>69.18</td>
<td></td>
</tr>
</tbody>
</table>

\(^{1}\text{KINETICS}\) ** QCISDT

The average heat of formation is 23.78 kcal mol\(^{-1}\) with a standard deviation of 0.61 kcal mol\(^{-1}\). All values in Table VII are within two standard deviations of the average. Optimisation of the groups results in a heat of formation of 24.03 kcal mol\(^{-1}\).

The average molar entropy is 69.25 cal K\(^{-1}\) mol\(^{-1}\) with a standard deviation of 0.72 cal K\(^{-1}\) mol\(^{-1}\). All of the literature values in Table VIII are within two standard deviations of the average. Optimisation of the groups results in an entropy of 69.18 cal K\(^{-1}\) mol\(^{-1}\).

5. \textit{iso-Propyl radical}

The heats of formation values are shown in Tables IX while molar entropy values are included in Table X.

The average heat of formation of the \textit{iso}\text{-}propyl radical is 20.89 kcal K\(^{-1}\) mol\(^{-1}\) with a standard deviation of 0.97 kcal mol\(^{-1}\). Values that differ from the average by more than two standard deviations include the value from Holmes \textit{et al.}\(^{29}\) which is 1.80 cal K\(^{-1}\) mol\(^{-1}\) smaller than the average. When this value is excluded

average becomes 20.77 kcal K\(^{-1}\) mol\(^{-1}\). Optimisation of the groups results in a heat of formation of 20.95 kcal K\(^{-1}\) mol\(^{-1}\).

The average molar entropy is 69.02 cal K\(^{-1}\) mol\(^{-1}\) with a standard deviation of 0.81 cal K\(^{-1}\) mol\(^{-1}\). Values that differ from the average by more than two deviations include the recommendation from Seetula and Slagle\(^{30}\) which is 1.86 cal K\(^{-1}\) mol\(^{-1}\) less than the average. Excluding this value results in an average of 69.24 cal K\(^{-1}\) mol\(^{-1}\) which is 0.49 cal K\(^{-1}\) mol\(^{-1}\) larger than the value of 68.75 cal K\(^{-1}\) mol\(^{-1}\) estimated using group additivity after optimisation.

6. \textit{n-Butane}

There is relatively good agreement among the literature values for both the heat of formation and molar entropy of \textit{n}\text{-}butane as shown in Tables XI and XII, respectively.

The average heat of formation for \textit{n}\text{-}butane is 29.99 kcal mol\(^{-1}\) with a standard deviation of 0.17 kcal
mol$^{-1}$. The Rayne and Forest$^{19}$ recommendation differs from the average by 0.45 kcal mol$^{-1}$ which is more than two standards deviation. When it is excluded the average becomes −30.04 kcal mol$^{-1}$. Optimisation of the groups results in a heat of formation of −30.02 kcal mol$^{-1}$.

The average molar entropy of $n$-butane is 74.05 cal K$^{-1}$ mol$^{-1}$ with a standard deviation of 0.17 cal K$^{-1}$ mol$^{-1}$. All of the literature values in Table XII are within two deviations of the average. After optimisation the heat of formation is 74.14 cal K$^{-1}$ mol$^{-1}$ which is 0.09 cal mol$^{-1}$ larger than the average.

7. **iso-Butane**

As with the values for the heat of formation and molar entropy for $n$-butane there is also good agreement in the literature for the other C$_3$H$_8$ isomer, iso-butane as shown in Tables XIII and XIV.

The average heat of formation of iso-butane is −32.09 kcal mol$^{-1}$ with a standard deviation of 0.24 kcal mol$^{-1}$. The measured value from the 1945 study by Prosen and Rossini$^{13}$ differs from the average by 0.64 kcal mol$^{-1}$ which is more than twice the standard deviation. When it is excluded the average becomes −32.16 kcal mol$^{-1}$. Optimisation of the groups results in a heat of formation of −32.17 kcal mol$^{-1}$.

The average molar entropy of iso-butane is 70.70 cal K$^{-1}$ mol$^{-1}$ with a standard deviation of 0.27 cal K$^{-1}$ mol$^{-1}$. All of the values in Table XIV agree with the average within twice the standard deviation.

8. **n-Butyl radical**

![n-Butyl radical structure]

Tables XV and XVI include values for heats of formation and molar entropies for the $n$-butyl radical respectively. There is good agreement amongst the literature values for the heat of formation (Table XV). The agreement is less favourable amongst the relatively few molar entropy values (Table XVI). The recommendation from the Third Millennium Thermodynamic Database$^3$ is 4.10 cal K$^{-1}$ mol$^{-1}$ smaller than the average.

The average literature heat of formation for the $n$-butyl radical is 19.26 kcal mol$^{-1}$ with a standard deviation of 0.60 kcal mol$^{-1}$. All of the values in Table XV agree...
The average molar entropy of the \( n \)-butyl radical is 77.87 cal K\(^{-1}\) mol\(^{-1}\) with a standard deviation of 1.98 cal K\(^{-1}\) mol\(^{-1}\). The recommendation from the \( 3^{rd} \)Millennium database\(^3 \) differs from the average by 4.35 cal K\(^{-1}\) mol\(^{-1}\) which is more than twice the standard deviation. When it is excluded the average becomes 78.74 cal K\(^{-1}\) mol\(^{-1}\). Optimisation of the groups results in a standard molar entropy of 78.83 cal K\(^{-1}\) mol\(^{-1}\).

### 9. \( s \)-Butyl radical

Tables XVII and XVIII include values for heats of formation and molar entropies for the \( s \)-butyl radical respectively. Similar to the \( n \)-butyl radical there is relatively good agreement amongst the values for the heat of formation while the recommendation from the Third Millennium Thermodynamic Database\(^3 \) is significantly smaller than the other values.

The average heat of formation for the \( s \)-butyl radical is 15.83 kcal mol\(^{-1}\) with a standard deviation of 0.84 kcal mol\(^{-1}\). The value from Castelhano and Griller\(^{28} \) differs from the average by 2.03 kcal mol\(^{-1}\) which is more than twice the standard deviation and when it is excluded the average becomes 16.11 kcal mol\(^{-1}\). Optimisation of the groups results in a heat of formation of 15.95 kcal mol\(^{-1}\).

The average molar entropy of the \( s \)-butyl radical is 79.34 cal K\(^{-1}\) mol\(^{-1}\) with a standard deviation of 1.52 cal K\(^{-1}\) mol\(^{-1}\). All of the values in Table XVIII agree with the average within twice the standard deviation. Optimisation of the groups results in a standard molar entropy of 79.77 cal K\(^{-1}\) mol\(^{-1}\).

### 10. \( iso \)-Butyl radical

Values for the heat of formation and molar entropy for the \( iso \)-butyl radical are included in Tables XIX and XX. Similar to \( n \)- and \( s \)-butyl radicals there is good agreement overall while the the recommendation from the Third Millennium Thermodynamic Database for molar entropy differs significantly from the other literature values.

The average heat of formation for the \( iso \)-butyl radical is 17.10 kcal mol\(^{-1}\) with a standard deviation of 0.63 kcal mol\(^{-1}\). The experimental value recommended by Holmes \( et \ al.\)\(^{29} \) differs from the average by 1.30 kcal mol\(^{-1}\) which
The average molar entropy becomes 11 than twice the standard deviation when it is excluded the average by 3.01 kcal mol\(^{-1}\). There is relatively good agreement amongst the values for the molar entropy in the literature.

The average heat of formation for tert-butyl radical is 11.71 kcal mol\(^{-1}\) with a standard deviation of 1.27 kcal mol\(^{-1}\). The recommendation from McMillen and Golden differs from the average by 3.01 kcal mol\(^{-1}\) which is more than twice the standard deviation when it is excluded the average becomes 11.86 kcal mol\(^{-1}\).

The average molar entropy is 75.84 cal K\(^{-1}\) mol\(^{-1}\) with a standard deviation of 0.79 cal K\(^{-1}\) mol\(^{-1}\). All of the values in Table XXII agree with the average within twice the standard deviation.

### 11. tert-Butyl radical

Values for the heat of formation and molar entropy for the tert-butyl radical are included in Tables XXI and XXII. There are several studies in the literature that recommended values for the heat of formation of tert-butyl radical. The values vary from 8.70 kcal mol\(^{-1}\) to 13.62 kcal mol\(^{-1}\). There is relatively good agreement amongst the values for the molar entropy in the literature.

The average heat of formation for tert-butyl radical is 11.71 kcal mol\(^{-1}\) with a standard deviation of 1.27 kcal mol\(^{-1}\). The recommendation from McMillen and Golden differs from the average by 3.01 kcal mol\(^{-1}\) which is more than twice the standard deviation when it is excluded the average becomes 11.86 kcal mol\(^{-1}\).

The average molar entropy is 75.84 cal K\(^{-1}\) mol\(^{-1}\) with a standard deviation of 0.79 cal K\(^{-1}\) mol\(^{-1}\). All of the values in Table XXII agree with the average within twice the standard deviation.

### B. Alkenes and alkenyl radicals

#### 1. Ethylene

There is good agreement among the literature values for the heat of formation for ethylene within the literature as shown in Table XXIII. There are fewer values available for the molar entropy but there is good agreement among those available (Table XXIV).

The average heat of formation for ethylene is 12.53
There are several studies within the literature that provide values for the heats of formation for the vinyl radical as shown in Table XXV. The values range from 63.66 kcal mol\(^{-1}\) to 72.04 kcal mol\(^{-1}\). There are relatively few studies that report values for the molar entropy but there is good agreement amongst the ones that do.

The average heat of formation for the ethenyl or vinyl radical is 69.78 kcal mol\(^{-1}\) with a standard deviation of 2.57 kcal mol\(^{-1}\). The value from Lies et al.\(^{36}\) differs from the average by 6.45 kcal mol\(^{-1}\) which is more than twice the standard deviation and when it is excluded the average becomes 70.36 kcal mol\(^{-1}\). Optimisation of the groups results in a heat of formation of 70.09 kcal mol\(^{-1}\).

The average molar entropy for ethylene is 52.38 cal K\(^{-1}\) mol\(^{-1}\) with a standard deviation of 0.03 cal K\(^{-1}\) mol\(^{-1}\). All of the values in Table XXIV agree with the average within twice the standard deviation. After optimisation the group additivity approach estimates a value of 52.43 cal K\(^{-1}\) mol\(^{-1}\).

**2. Ethenyl/vinyl Radical**

\[ \text{H}_2\text{C} = \text{CH} \]

There are several studies within the literature that provide values for the heats of formation for the vinyl radical as shown in Table XXV. The values range from 63.66 kcal mol\(^{-1}\) to 72.04 kcal mol\(^{-1}\). There are relatively few studies that report values for the molar entropy but there is good agreement amongst the ones that do.

The average heat of formation for the ethenyl or vinyl radical is 69.78 kcal mol\(^{-1}\) with a standard deviation of 2.57 kcal mol\(^{-1}\). The value from Lies et al.\(^{36}\) differs from the average by 6.45 kcal mol\(^{-1}\) which is more than twice the standard deviation and when it is excluded the average becomes 70.36 kcal mol\(^{-1}\). Optimisation of the groups results in a heat of formation of 70.09 kcal mol\(^{-1}\).

The average molar entropy for the vinyl radical is 55.96 cal K\(^{-1}\) mol\(^{-1}\) with a standard deviation of 0.22 cal K\(^{-1}\) mol\(^{-1}\). All of the values in Table XXVI agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is 56.34 cal K\(^{-1}\) mol\(^{-1}\).

**3. Propene**

\[ \text{H}_3\text{C} - \text{CH}_2 \]

Values for the heat of formation of propene vary from 3.72\(^{19}\) to 5.60\(^{18}\) kcal mol\(^{-1}\) as shown in Table XXVII. There is relatively good agreement among the limited values available for the molar entropy of propene as shown

**TABLE XXIII. Enthalpy of formation (kcal mol\(^{-1}\)) of ethylene.**

<table>
<thead>
<tr>
<th>Literature</th>
<th>(\Delta H^\circ)</th>
<th>Year Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chao and Zwolinski(^{12})</td>
<td>12.55</td>
<td>1975 Calc.(^*)</td>
</tr>
<tr>
<td>Chase(^{45})</td>
<td>12.54</td>
<td>1998 Rev.</td>
</tr>
<tr>
<td>Lange’s Handbook(^{21})</td>
<td>12.50</td>
<td>1999 Rev.</td>
</tr>
<tr>
<td>Baulch et al.(^{17})</td>
<td>12.50</td>
<td>2005 Rev.</td>
</tr>
<tr>
<td>Rayne and Forest(^{19})</td>
<td>12.57</td>
<td>2010 Calc.(^**)</td>
</tr>
<tr>
<td>Rayne and Forest(^{19})</td>
<td>11.95</td>
<td>2010 Calc.(^†)</td>
</tr>
<tr>
<td>CRC(^{22})</td>
<td>12.52</td>
<td>2011 Rev.</td>
</tr>
<tr>
<td>3(^{rd})Millennium(^{3})</td>
<td>12.5</td>
<td>2012</td>
</tr>
<tr>
<td>Goldsmith et al.(^{4})</td>
<td>12.50 ±0.10</td>
<td>2012 Calc.(^†)</td>
</tr>
<tr>
<td>ATcT(^2)</td>
<td>12.56 ±0.04</td>
<td>2012 Calc.(^.§)</td>
</tr>
<tr>
<td>Verevkin et al.(^{5})</td>
<td>12.55</td>
<td>2013 Rev.</td>
</tr>
</tbody>
</table>

**Recommendation** 12.53

* GA

**TABLE XXIV. Molar entropy (cal K\(^{-1}\) mol\(^{-1}\)) of ethylene.**

<table>
<thead>
<tr>
<th>Literature</th>
<th>(S^\circ)</th>
<th>Year Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chase(^{35})</td>
<td>52.42</td>
<td>1998 Rev.</td>
</tr>
<tr>
<td>Lange’s Handbook(^{21})</td>
<td>52.34</td>
<td>1999 Rev.</td>
</tr>
<tr>
<td>Baulch et al.(^{17})</td>
<td>52.40</td>
<td>2005 Rev.</td>
</tr>
<tr>
<td>CRC(^{22})</td>
<td>52.41</td>
<td>2011 Rev.</td>
</tr>
<tr>
<td>3(^{rd})Millennium(^{3})</td>
<td>52.42</td>
<td>2012</td>
</tr>
<tr>
<td>Goldsmith et al.(^{4})</td>
<td>52.30 ±0.40</td>
<td>2012 Calc.(^*)</td>
</tr>
</tbody>
</table>

**Standard Deviation** 0.05

**Recommendation** 52.38

* GA

**TABLE XXV. Enthalpy of formation (kcal mol\(^{-1}\)) of ethenyl radical.**

<table>
<thead>
<tr>
<th>Literature</th>
<th>(\Delta H^\circ)</th>
<th>Year Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lies et al.(^{36})</td>
<td>63.33</td>
<td>1988 Rev.</td>
</tr>
<tr>
<td>Parmar and Benson(^{47})</td>
<td>66.90 ±0.41</td>
<td>1988 Exp.(^*)</td>
</tr>
<tr>
<td>Russell et al.(^{48})</td>
<td>67.10 ±0.60</td>
<td>1989 Exp.(^*)</td>
</tr>
<tr>
<td>Berkowitz et al.(^{41})</td>
<td>71.60 ±0.79</td>
<td>1994 Rev.</td>
</tr>
<tr>
<td>Kaiser and Wallington(^{49})</td>
<td>70.60 ±0.40</td>
<td>1996 Exp.(^*)</td>
</tr>
<tr>
<td>Knyazev and Slagle(^{50})</td>
<td>71.39 ±1.60</td>
<td>1996 Calc.(^*)</td>
</tr>
<tr>
<td>Tsang(^{25})</td>
<td>71.60 ±1.20</td>
<td>1996 Rev.</td>
</tr>
<tr>
<td>Glakhovtsev and Bach(^{51})</td>
<td>72.04</td>
<td>1998 Calc.(^**)</td>
</tr>
<tr>
<td>Lange’s Handbook(^{21})</td>
<td>69.10</td>
<td>1999 Rev.</td>
</tr>
<tr>
<td>Baulch et al.(^{17})</td>
<td>71.60</td>
<td>2005 Rev.</td>
</tr>
<tr>
<td>Tabor et al.(^{52})</td>
<td>71.06 ±0.31</td>
<td>2012 Calc.(^†)</td>
</tr>
<tr>
<td>3(^{rd})Millennium(^{3})</td>
<td>70.88</td>
<td>2012 Calc.(^†)</td>
</tr>
<tr>
<td>Goldsmith et al.(^{4})</td>
<td>71.20 ±0.20</td>
<td>2012 Calc.(^†)</td>
</tr>
</tbody>
</table>

**Standard Deviation** 0.22

**Recommendation** 70.36

* KINETICS

**TABLE XXVI. Molar entropy (cal K\(^{-1}\) mol\(^{-1}\)) of ethenyl radical.**

<table>
<thead>
<tr>
<th>Literature</th>
<th>(S^\circ)</th>
<th>Year Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Russell et al.(^{36})</td>
<td>55.90 ±2.60</td>
<td>1989 Exp.(^*)</td>
</tr>
<tr>
<td>Lange’s Handbook(^{21})</td>
<td>56.40</td>
<td>1999 Rev.</td>
</tr>
<tr>
<td>Baulch et al.(^{17})</td>
<td>55.90</td>
<td>2005 Rev.</td>
</tr>
<tr>
<td>3(^{rd})Millennium(^{3})</td>
<td>55.85</td>
<td>2012</td>
</tr>
<tr>
<td>Goldsmith et al.(^{4})</td>
<td>55.85 ±0.20</td>
<td>2012 Calc.(^**)</td>
</tr>
</tbody>
</table>

**Standard Deviation** 0.22

**Recommendation** 55.96

* KINETICS

**TABLE XXVII. Molar entropy (cal K\(^{-1}\) mol\(^{-1}\)) of propene.**

<table>
<thead>
<tr>
<th>Literature</th>
<th>(S^\circ)</th>
<th>Year Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chao and Zwolinski(^{12})</td>
<td>3.72</td>
<td>1975 Calc.(^*)</td>
</tr>
<tr>
<td>Chase(^{45})</td>
<td>5.60</td>
<td>1998 Rev.</td>
</tr>
<tr>
<td>Lange’s Handbook(^{21})</td>
<td>3.72</td>
<td>1999 Rev.</td>
</tr>
<tr>
<td>Baulch et al.(^{17})</td>
<td>5.60</td>
<td>2005 Rev.</td>
</tr>
<tr>
<td>CRC(^{22})</td>
<td>3.72</td>
<td>2011 Rev.</td>
</tr>
<tr>
<td>3(^{rd})Millennium(^{3})</td>
<td>3.72</td>
<td>2012</td>
</tr>
<tr>
<td>Goldsmith et al.(^{4})</td>
<td>3.72</td>
<td>2013 Calc.(^*)</td>
</tr>
</tbody>
</table>

**Standard Deviation** 0.05

**Recommendation** 3.72

* KINETICS
The average heat of formation for propene is 4.92 kcal mol$^{-1}$ with a standard deviation of 0.43 kcal mol$^{-1}$. The value from Kollais et al.\textsuperscript{18} differs from the average by 0.68 kcal mol$^{-1}$ which is more than twice the standard deviation. When it is excluded the average becomes 4.68 kcal mol$^{-1}$. Optimisation of the groups results in a heat of formation of 4.92 kcal mol$^{-1}$.

The average molar entropy is 63.64 cal K$^{-1}$ mol$^{-1}$ with a standard deviation of 0.09 cal K$^{-1}$ mol$^{-1}$. All of the values in Table XXVIII agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is 63.53 cal K$^{-1}$ mol$^{-1}$.

### 4. Allyl radical

There are numerous studies that report values for the heat of formation for the allyl radical and there is good agreement among the recommendations in the literature as shown in Table XXIX. There is also good agreement among the molar entropy values as shown in Table XXX.

The average heat of formation for the allyl radical is 40.16 kcal mol$^{-1}$ with a standard deviation of 0.63 kcal mol$^{-1}$. All of the values in Table XXIX agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is 40.72 kcal mol$^{-1}$.

The average molar entropy is 62.24 cal K$^{-1}$ mol$^{-1}$ with a standard deviation of 0.55 cal K$^{-1}$ mol$^{-1}$. All of the values in Table XXX agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is 65.56 cal K$^{-1}$ mol$^{-1}$.

### 5. 1-Propenyl radical

The heat of formation and molar entropy for 1-propenyl radical has been reported in a limited number of studies\textsuperscript{4,17,58,59} and values are included in Tables XXXI and XXXII. Further studies are needed to acquire a more accurate estimate of the uncertainty for these parame-

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**TABLE XXVII. Enthalpy of formation (kcal mol$^{-1}$) of propene.**

<table>
<thead>
<tr>
<th>Literature</th>
<th>$\Delta_f H^\circ$</th>
<th>Year</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lange’s Handbook\textsuperscript{24}</td>
<td>63.72</td>
<td>1999</td>
<td>Rev.</td>
</tr>
<tr>
<td>Baulch et al.\textsuperscript{17}</td>
<td>63.70</td>
<td>2005</td>
<td>Calc.</td>
</tr>
<tr>
<td>3rd Millennium\textsuperscript{3}</td>
<td>63.73</td>
<td>2012</td>
<td></td>
</tr>
<tr>
<td>Goldsmith et al.\textsuperscript{4}</td>
<td>63.60 ±0.90</td>
<td>2012</td>
<td>Calc.</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Recommendation</td>
<td>63.64</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GA</td>
<td>63.53</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TABLE XXVIII. Molar entropy (cal K$^{-1}$ mol$^{-1}$) of propene.**

<table>
<thead>
<tr>
<th>Literature</th>
<th>$\Delta_f H^\circ$</th>
<th>Year</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Horiyan et al.\textsuperscript{23}</td>
<td>4.88</td>
<td>1975</td>
<td>Exp.</td>
</tr>
<tr>
<td>Lange’s Handbook\textsuperscript{24}</td>
<td>4.78</td>
<td>1999</td>
<td>Rev.</td>
</tr>
<tr>
<td>Kollais et al.\textsuperscript{18}</td>
<td>5.60</td>
<td>2005</td>
<td>Calc.</td>
</tr>
<tr>
<td>Baulch et al.\textsuperscript{17}</td>
<td>4.80</td>
<td>2005</td>
<td>Calc.</td>
</tr>
<tr>
<td>Rayne and Forest\textsuperscript{19}</td>
<td>5.04</td>
<td>2010</td>
<td>Calc.</td>
</tr>
<tr>
<td>Rayne and Forest\textsuperscript{19}</td>
<td>3.72</td>
<td>2010</td>
<td>Calc.</td>
</tr>
<tr>
<td>CRC\textsuperscript{22}</td>
<td>4.78</td>
<td>2011</td>
<td>Rev.</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.43</td>
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<td></td>
</tr>
<tr>
<td>Recommendation</td>
<td>4.68</td>
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<tr>
<td>GA</td>
<td>4.92</td>
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</tr>
</tbody>
</table>

**TABLE XXIX. Enthalpy of formation (kcal mol$^{-1}$) of allyl radical.**

<table>
<thead>
<tr>
<th>Literature</th>
<th>$\Delta_f H^\circ$</th>
<th>Year</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rossi and Golden\textsuperscript{24}</td>
<td>39.50 ±1.50</td>
<td>1979</td>
<td>Exp.</td>
</tr>
<tr>
<td>Traeger\textsuperscript{25}</td>
<td>40.50</td>
<td>1984</td>
<td>Exp.</td>
</tr>
<tr>
<td>Tsang\textsuperscript{25}</td>
<td>40.90</td>
<td>1996</td>
<td>Rev.</td>
</tr>
<tr>
<td>Baulch et al.\textsuperscript{17}</td>
<td>40.50</td>
<td>2005</td>
<td>Rev.</td>
</tr>
<tr>
<td>Lee and Bozzelli\textsuperscript{56}</td>
<td>40.50</td>
<td>2005</td>
<td>Calc.</td>
</tr>
<tr>
<td>Tabor et al.\textsuperscript{52}</td>
<td>40.55</td>
<td>2012</td>
<td>Calc.</td>
</tr>
<tr>
<td>3rd Millennium\textsuperscript{3}</td>
<td>39.50</td>
<td>2012</td>
<td>Calc.</td>
</tr>
<tr>
<td>Cord et al.\textsuperscript{57}</td>
<td>39.10</td>
<td>2012</td>
<td>Calc.</td>
</tr>
<tr>
<td>Goldsmith et al.\textsuperscript{4}</td>
<td>40.60 ±0.90</td>
<td>2012</td>
<td>Calc.</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.63</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Recommendation</td>
<td>40.16</td>
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<tr>
<td>GA</td>
<td>40.72</td>
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</tbody>
</table>

**TABLE XXX. Molar entropy (cal K$^{-1}$ mol$^{-1}$) of allyl radical.**

<table>
<thead>
<tr>
<th>Literature</th>
<th>$\Delta_f H^\circ$</th>
<th>Year</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Horiyan et al.\textsuperscript{23}</td>
<td>6.6</td>
<td>1975</td>
<td>Exp.</td>
</tr>
<tr>
<td>Lange’s Handbook\textsuperscript{24}</td>
<td>6.00</td>
<td>2005</td>
<td>Rev.</td>
</tr>
<tr>
<td>Baulch et al.\textsuperscript{17}</td>
<td>6.00</td>
<td>2005</td>
<td>Rev.</td>
</tr>
<tr>
<td>3rd Millennium\textsuperscript{3}</td>
<td>6.00</td>
<td>2012</td>
<td></td>
</tr>
<tr>
<td>Goldsmith et al.\textsuperscript{4}</td>
<td>6.55 ±0.80</td>
<td>2012</td>
<td>Calc.</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.55</td>
<td></td>
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</tr>
<tr>
<td>Recommendation</td>
<td>62.24</td>
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</tr>
<tr>
<td>GA</td>
<td>62.56</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

\textsuperscript{1} Kinetics
\textsuperscript{2} PMS
\textsuperscript{3} B3LYP
\textsuperscript{4} HEAT
\textsuperscript{5} CBS-QB3
\textsuperscript{6} QCISDT
a standard deviation of 0.63. The value estimated using group additivity after optimisation is 64.69 cal K⁻¹ mol⁻¹. All of the values in Table XXXIII agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is 64.50 cal K⁻¹ mol⁻¹.

7. 1-Butene

Enthalpies of formation and molar entropies for 1-butene are included in Tables XXXV and XXXVI respectively. There is relatively good agreement among the available values.

The average heat of formation for 1-butene is −0.06 kcal mol⁻¹ with a standard deviation of 0.06 kcal mol⁻¹. The two values in Table XXXIV agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is 64.84 cal K⁻¹ mol⁻¹.

TABLE XXXI. Enthalpy of formation (kcal mol⁻¹) of 1-propenyl radical.

<table>
<thead>
<tr>
<th>Literature</th>
<th>Δ₁H</th>
<th>Year Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wu and Kern⁹⁹</td>
<td>62.80</td>
<td>187 Exp.****</td>
</tr>
<tr>
<td>Baulch et al.¹⁷</td>
<td>62.80</td>
<td>2005 Rev.</td>
</tr>
<tr>
<td>3rd Millennium³</td>
<td>63.46</td>
<td>2012</td>
</tr>
<tr>
<td>Goldsmith et al.³</td>
<td>64.10</td>
<td>2012 Calc.</td>
</tr>
<tr>
<td>Standard Deviation 0.54</td>
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<td></td>
</tr>
<tr>
<td>Recommendation 63.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GA</td>
<td>63.35</td>
<td></td>
</tr>
</tbody>
</table>

* KINETICS  ** QCISDT

TABLE XXXII. Molar entropy (cal K⁻¹ mol⁻¹) of 1-propenyl radical.

<table>
<thead>
<tr>
<th>Literature</th>
<th>S°</th>
<th>Year Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baulch et al.¹⁷</td>
<td>64.80</td>
<td>2005 Rev.</td>
</tr>
<tr>
<td>3rd Millennium³</td>
<td>64.84</td>
<td>2012</td>
</tr>
<tr>
<td>Goldsmith et al.³</td>
<td>94.90</td>
<td>2012 Calc.</td>
</tr>
<tr>
<td>Standard Deviation 0.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Recommendation 64.86</td>
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<tr>
<td>GA</td>
<td>64.69</td>
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</tbody>
</table>

* QCISDT

TABLE XXXIII. Enthalpy of formation (kcal mol⁻¹) of 2-propenyl radical.

<table>
<thead>
<tr>
<th>Literature</th>
<th>Δ₁H</th>
<th>Year Source</th>
</tr>
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<tbody>
<tr>
<td>Wu and Kern⁹⁹</td>
<td>56.80</td>
<td>1987 Exp.****</td>
</tr>
<tr>
<td>3rd Millennium³</td>
<td>56.80</td>
<td>2012 Calc.</td>
</tr>
<tr>
<td>Goldsmith et al.³</td>
<td>58.03</td>
<td>2012 Calc.</td>
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<tr>
<td>Standard Deviation 1.74</td>
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<tr>
<td>Recommendation 58.03</td>
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<tr>
<td>GA</td>
<td>59.78</td>
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* KINETICS  ** QCISDT

TABLE XXXIV. Molar entropy (cal K⁻¹ mol⁻¹) of 2-propenyl radical.

<table>
<thead>
<tr>
<th>Literature</th>
<th>Δ₁H</th>
<th>Year Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>3rd Millennium³</td>
<td>63.59</td>
<td>2012</td>
</tr>
<tr>
<td>Goldsmith et al.³</td>
<td>65.40</td>
<td>2012 Calc.</td>
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<td>Standard Deviation 0.91</td>
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<td>Recommendation 64.50</td>
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<td>GA</td>
<td>64.84</td>
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</tbody>
</table>

* QCISDT

TABLE XXXV. Enthalpy of formation (kcal mol⁻¹) of 1-butene.

<table>
<thead>
<tr>
<th>Literature</th>
<th>Δ₁H</th>
<th>Year Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prosen et al.⁶⁰</td>
<td>−0.15</td>
<td>1951 Exp.⁹⁹</td>
</tr>
<tr>
<td>Traeger et al.⁵⁵</td>
<td>−0.09</td>
<td>1984 Exp.**</td>
</tr>
<tr>
<td>Lange’s Handbook²¹</td>
<td>−0.02</td>
<td>1999 Rev.</td>
</tr>
<tr>
<td>Baulch et al.¹⁷</td>
<td>0.00</td>
<td>2005 Rev.</td>
</tr>
<tr>
<td>CRC²²</td>
<td>0.10</td>
<td>2011 Rev.</td>
</tr>
<tr>
<td>3rd Millennium³</td>
<td>−0.01</td>
<td>2012</td>
</tr>
<tr>
<td>Goldsmith et al.³</td>
<td>−0.00 ±0.10</td>
<td>2012 Calc.†</td>
</tr>
<tr>
<td>ATcT²</td>
<td>−0.07 ±0.11</td>
<td>2012 Calc.†</td>
</tr>
<tr>
<td>Verevkin</td>
<td>−0.14</td>
<td>2013 Rev.</td>
</tr>
<tr>
<td>Standard Deviation 0.06</td>
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<tr>
<td>Recommendation −0.06</td>
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<tr>
<td>GA</td>
<td>−0.05</td>
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</tbody>
</table>

* CALORIMETRY  ** PMS  † QCISDT  † TN

TABLE XXXV. Enthalpy of formation (kcal mol⁻¹) of 1-butene.

As with 1-propenyl radical there are only a limited number of studies that report values for the heat of formation for the 2-propenyl radical. In order for a group additivity approach to be effective for the estimation of thermochemical properties for alkenyl radicals further study of these radicals is required.

The average heat of formation of the 2-propenyl radical is 58.03 kcal mol⁻¹ with a standard deviation of 1.74 kcal mol⁻¹. All of the values in Table XXXIII agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is 59.78 kcal mol⁻¹.

The average molar entropy is 64.50 cal K⁻¹ mol⁻¹ with a standard deviation of 0.91 cal K⁻¹ mol⁻¹. The two values in Table XXXIV agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is 64.84 cal K⁻¹ mol⁻¹.
All of the values in Table XXXV agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is −0.05 kcal mol⁻¹.

The average molar entropy is 73.21 cal K⁻¹ mol⁻¹ with a standard deviation of 0.24 cal K⁻¹ mol⁻¹. All of the values in Table XXXVI agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is 73.08 cal K⁻¹ mol⁻¹.

### TABLE XXXVII. Enthalpy of formation (kcal mol⁻¹) of 2-butene.

<table>
<thead>
<tr>
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<th>Δ_H°F</th>
<th>Year Source</th>
<th>Source</th>
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</thead>
<tbody>
<tr>
<td>Prosen et al.⁶⁶</td>
<td>−2.58</td>
<td>1951 Exp</td>
<td>PMS</td>
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<tr>
<td>Traeger et al.⁵⁵</td>
<td>−2.91</td>
<td>1984 Exp**</td>
<td>TN</td>
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<tr>
<td>Lange’s Handbook²¹</td>
<td>−2.72</td>
<td>1999 Rev.</td>
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<tr>
<td>Baulch et al.¹⁷</td>
<td>−2.70</td>
<td>2005 Rev.</td>
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</tr>
<tr>
<td>CRC²²</td>
<td>−2.725</td>
<td>2011 Rev.</td>
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<tr>
<td>3rd Millennium³</td>
<td>−2.67</td>
<td>2012</td>
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<tr>
<td>Goldsmith et al.⁴</td>
<td>−2.70 ±0.20 2012 Calc.†</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ATcT²</td>
<td>−2.67 ±0.12 2012 Calc.‡</td>
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<td></td>
</tr>
<tr>
<td>Verevkin⁵</td>
<td>−2.56</td>
<td>2013 Rev.</td>
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</tr>
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<td><strong>CALORIMETRY</strong></td>
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<tr>
<td><strong>PMS</strong></td>
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</tr>
<tr>
<td><strong>QCISDT</strong></td>
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<td></td>
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</tr>
<tr>
<td><strong>TN</strong></td>
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### TABLE XXXVIII. Molar entropy (cal K⁻¹ mol⁻¹) of 2-butene.

<table>
<thead>
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<th>Literature</th>
<th>S°F</th>
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<th>Source</th>
</tr>
</thead>
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<tr>
<td>Lange’s Handbook²¹</td>
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<td>PMS</td>
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<tr>
<td>Baulch et al.¹⁷</td>
<td>73.60</td>
<td>2005 Rev.</td>
<td>TN</td>
</tr>
<tr>
<td>3rd Millennium³</td>
<td>72.98</td>
<td>2012</td>
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<tr>
<td>Goldsmith et al.⁴</td>
<td>73.20±1.50 2012 Calc.*</td>
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<td>Standard Deviation</td>
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</tr>
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<td><strong>Recommendation</strong></td>
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</table>

### TABLE XXXIX. Enthalpy of formation (kcal mol⁻¹) of iso-butene.

<table>
<thead>
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<th>Literature</th>
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<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prosen et al.⁶⁶</td>
<td>−4.29</td>
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<td>PMS</td>
</tr>
<tr>
<td>Traeger et al.⁵⁵</td>
<td>−4.04</td>
<td>1984 Exp**</td>
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<td>Baulch et al.¹⁷</td>
<td>−4.00</td>
<td>2005 Rev.</td>
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<tr>
<td>CRC²²</td>
<td>−4.04</td>
<td>2011 Rev.</td>
<td></td>
</tr>
<tr>
<td>3rd Millennium³</td>
<td>−4.20</td>
<td>2012</td>
<td></td>
</tr>
<tr>
<td>Goldsmith et al.⁴</td>
<td>−4.10 ±0.20 2012 Calc.†</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ATcT²</td>
<td>−4.20 ±0.13 2012 Calc.‡</td>
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</tr>
<tr>
<td>Verevkin⁵</td>
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<td>2013 Rev.</td>
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<td><strong>PMS</strong></td>
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</tr>
<tr>
<td><strong>TN</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### TABLE XXXX. Enthalpy of formation (kcal mol⁻¹) of iso-butene.

The average molar entropy is 70.77 cal K⁻¹ mol⁻¹ with a standard deviation of 0.07 cal K⁻¹ mol⁻¹. All of the values in Table XXXX agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is 70.50 cal K⁻¹ mol⁻¹.

### 9. iso-Butene

Values for the heat of formation of iso-butene are in good agreement and are in the range of −4.29 to −4.00 kcal mol as shown in Table XXXX.

The average heat of formation for iso-butene is −4.16 kcal mol⁻¹ with a standard deviation of 0.11 kcal mol⁻¹. All of the values in Table XXXX agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is −4.08 kcal mol⁻¹.

The average molar entropy of iso-butene is 70.01 cal K⁻¹ mol⁻¹ with a standard deviation of 0.66 cal K⁻¹ mol⁻¹. The value from the Third Millennium Thermodynamic Database³ differs from the average by 1.31 cal K⁻¹ mol⁻¹ which is more than twice the standard deviation. When this value is excluded the average becomes 70.16 cal K⁻¹ mol⁻¹. The value estimated using group additivity after optimi-
for 1-buten-1-yl radical is 74.60 cal K$^{-1}$ mol$^{-1}$ using group additivity after optimisation is 58.38 kcal mol$^{-1}$ within twice the standard deviation. The value estimated using group additivity after optimisation is 72.24 cal K$^{-1}$ mol$^{-1}$. All three values in Table XLII agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is 58.38 kcal mol$^{-1}$. The average of the three heat of formation values available is 50.00 kcal mol$^{-1}$. All three values in Table XLIII agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is 72.24 cal K$^{-1}$ mol$^{-1}$. The average molar entropy is 73.92 cal K$^{-1}$ mol$^{-1}$ with a standard deviation of 0.29 kcal mol$^{-1}$ and all three values in Table XLIII agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is 52.14 kcal mol$^{-1}$. The average molar entropy is 73.92 cal K$^{-1}$ mol$^{-1}$ with a standard deviation of 1.02 cal K$^{-1}$ mol$^{-1}$ and all three values in Table XLIV agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is 73.18 cal K$^{-1}$ mol$^{-1}$.

### 10. 1-Buten-1-yl radical

There are very few studies that report values for the heat of formation for any of the C$_4$H$_7$ butenyl radicals. Further studies of these radicals are required.

The average of the three heat of formation values available for 1-buten-1-yl (1C$_4$H$_7$-1) radical is 59.05 kcal mol$^{-1}$ with a standard deviation of 0.22 kcal mol$^{-1}$ and all three values in Table XI agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is 58.38 kcal mol$^{-1}$.

The average of the three molar entropy values available for 1-buten-1-yl radical is 74.60 cal K$^{-1}$ mol$^{-1}$ with a standard deviation of 0.16 cal K$^{-1}$ mol$^{-1}$ and all three values in Table XL agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is 70.16 cal K$^{-1}$ mol$^{-1}$.

### 11. 2-Buten-2-yl radical

Values in the literature for the heat of formation for 2-buten-2-yl (2C$_4$H$_7$-2) radical range from 53.50$^{12}$ to 54.20$^{17}$ kcal mol$^{-1}$. The average of the three values is 53.83 kcal mol$^{-1}$ with a standard deviation of 0.29 kcal mol$^{-1}$. All three values in Table XLIII agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is 52.14 kcal mol$^{-1}$.

The average molar entropy is 73.92 cal K$^{-1}$ mol$^{-1}$ with a standard deviation of 1.02 cal K$^{-1}$ mol$^{-1}$. All three values in Table XLIV agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is 73.18 cal K$^{-1}$ mol$^{-1}$.

### 12. 3-Buten-1-yl radical

Similar to 1-buten-1-yl and 2-buten-2-yl radicals discussed above there are very few literature values in the literature for the heat of formation for 3-buten-1-yl (3C$_4$H$_7$-1) radical as shown in Table XLV. The average of the three heat of formation values available is 50.00 kcal mol$^{-1}$ with a standard deviation of 0.99 kcal mol$^{-1}$. The value estimated using group additivity after optimisation 

<table>
<thead>
<tr>
<th>Literature</th>
<th>$S^\circ$</th>
<th>Year Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baulch et al.$^{17}$</td>
<td>74.90</td>
<td>2005 Rev.</td>
</tr>
<tr>
<td>3$^{rd}$ Millennium$^3$</td>
<td>74.40</td>
<td>2012</td>
</tr>
<tr>
<td>Goldsmith et al.$^4$</td>
<td>74.50±1.50</td>
<td>2012 Calc.$^*$</td>
</tr>
<tr>
<td>Recommendation</td>
<td>74.60</td>
<td></td>
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<td>GA</td>
<td>74.24</td>
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</tr>
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</table>

TABLE XLII. Molar entropy (cal K$^{-1}$ mol$^{-1}$) of 1-buten-1-yl radical.

<table>
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<tr>
<th>Literature</th>
<th>$\Delta f H^\circ$</th>
<th>Year Source</th>
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<tbody>
<tr>
<td>Baulch et al.$^{17}$</td>
<td>74.90</td>
<td>2005 Rev.</td>
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<tr>
<td>3$^{rd}$ Millennium$^3$</td>
<td>74.40</td>
<td>2012</td>
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<tr>
<td>Goldsmith et al.$^4$</td>
<td>74.50±1.50</td>
<td>2012 Calc.$^*$</td>
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<td>74.60</td>
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<td>GA</td>
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<td>* QCISDT</td>
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TABLE XLIII. Enthalpy of formation (kcal mol$^{-1}$) of 2-buten-2-yl radical.

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<tr>
<th>Literature</th>
<th>$S^\circ$</th>
<th>Year Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baulch et al.$^{17}$</td>
<td>74.90</td>
<td>2005 Rev.</td>
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<tr>
<td>3$^{rd}$ Millennium$^3$</td>
<td>74.40</td>
<td>2012</td>
</tr>
<tr>
<td>Goldsmith et al.$^4$</td>
<td>74.50±1.50</td>
<td>2012 Calc.$^*$</td>
</tr>
<tr>
<td>Recommendation</td>
<td>74.60</td>
<td></td>
</tr>
<tr>
<td>GA</td>
<td>74.24</td>
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</tbody>
</table>

TABLE XLIV. Molar entropy (cal K$^{-1}$ mol$^{-1}$) of 2-buten-2-yl radical.

<table>
<thead>
<tr>
<th>Literature</th>
<th>$S^\circ$</th>
<th>Year Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baulch et al.$^{17}$</td>
<td>74.90</td>
<td>2005 Rev.</td>
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<td>Goldsmith et al.$^4$</td>
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<td>GA</td>
<td>74.24</td>
<td></td>
</tr>
<tr>
<td>* QCISDT</td>
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</table>

TABLE XLV. Molar entropy (cal K$^{-1}$ mol$^{-1}$) of 3-buten-1-yl radical.
is 49.00 kcal mol\(^{-1}\).

There is relatively good agreement between the recommendations for the standard molar entropy as shown in Table XLVI. The average of the values is 75.92 cal K\(^{-1}\) mol\(^{-1}\) with a standard deviation of 0.48 cal K\(^{-1}\) mol\(^{-1}\). All of the values in Table XLVI agree with the average within twice the standard deviation and the value estimated using group additivity after optimisation is 76.39 cal K\(^{-1}\) mol\(^{-1}\).

13. 2-Methylallyl radical

Unlike the other C\(_4\)H\(_7\) radicals there are several studies that report heat of formation values for 2-methylallyl radical as shown in Table XLVII. Table XLVIII shows that there are fewer values available for the molar entropy and furter study of this radical is recommended.

The average heat of formation for 2-methylallyl radical is 32.33 kcal mol\(^{-1}\) with a standard deviation of 2.31 kcal mol\(^{-1}\). All of the values in Table XLVII agree with the average within twice the standard deviation and the value estimated using group additivity after optimisation is 31.72 kcal mol\(^{-1}\).

The average molar entropy of 2-methylallyl radical from the recommendations of the 3\(^{rd}\)Millennium database and the study by Goldsmith \textit{et al.}\(^4\) is 71.05 cal K\(^{-1}\) mol\(^{-1}\) with a standard deviation of 0.84 cal K\(^{-1}\) mol\(^{-1}\). The value estimated using group additivity after optimisation is 70.57 cal K\(^{-1}\) mol\(^{-1}\).

14. 1-Methylallyl radical

The average heat of formation for 1-methylallyl radical is 33.08 kcal mol\(^{-1}\) with a standard deviation of 1.38 kcal mol\(^{-1}\). All of the values Table XLIX agree with the average within twice the standard deviation and the value estimated using group additivity after optimisation is 33.09 kcal mol\(^{-1}\).

### Table XLV. Enthalpy of formation (kcal mol\(^{-1}\)) of 3-en-1-yl radical.

<table>
<thead>
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<th>Literature</th>
<th>(\Delta_f H^\circ)</th>
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<th>Source</th>
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<td>Baulch \textit{et al.}(^3)</td>
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<td>3(^{rd})Millennium(^3)</td>
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<td>2012</td>
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<tr>
<td>Goldsmith \textit{et al.}(^4)</td>
<td>49.80±0.90</td>
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<tr>
<td><strong>Standard Deviation</strong></td>
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<tr>
<td><strong>GA</strong></td>
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<td></td>
</tr>
</tbody>
</table>

### Table XLVI. Molar entropy (cal K\(^{-1}\) mol\(^{-1}\)) of 3-en-1-yl radical.

<table>
<thead>
<tr>
<th>Literature</th>
<th>(S^\circ)</th>
<th>Year</th>
<th>Source</th>
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</thead>
<tbody>
<tr>
<td>Baulch \textit{et al.}(^3)</td>
<td>75.60</td>
<td>2005 Rev.</td>
<td></td>
</tr>
<tr>
<td>Miyoshi \textit{et al.}(^5)</td>
<td>76.72</td>
<td>2010 Calc.*</td>
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<td>3(^{rd})Millennium(^3)</td>
<td>75.85</td>
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<tr>
<td>Goldsmith \textit{et al.}(^4)</td>
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<td><strong>Recommendation</strong></td>
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### Table XLVII. Enthalpy of formation (kcal mol\(^{-1}\)) of 2-methylallyl radical.

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<th>Literature</th>
<th>(\Delta_f H^\circ)</th>
<th>Year</th>
<th>Source</th>
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<tbody>
<tr>
<td>Trethewey and Wrigley(^4)</td>
<td>30.00</td>
<td>1977 Exp*</td>
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</tr>
<tr>
<td>McMillen and Golden(^6)</td>
<td>28.56</td>
<td>1982 Rev.</td>
<td></td>
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<tr>
<td>Traeger(^5)</td>
<td>35.44</td>
<td>1986 Exp*</td>
<td></td>
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<td>Traeger(^6)</td>
<td>30.04</td>
<td>1989 Exp*</td>
<td></td>
</tr>
<tr>
<td>Lau \textit{et al.}(^7)</td>
<td>34.20±0.96</td>
<td>2007 Calc.(^1)</td>
<td></td>
</tr>
<tr>
<td>Agapito \textit{et al.}(^8)</td>
<td>34.18±0.96</td>
<td>2007 Calc.(^1)</td>
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<tr>
<td>3(^{rd})Millennium(^3)</td>
<td>32.89</td>
<td>2012</td>
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<tr>
<td>Goldsmith \textit{et al.}(^4)</td>
<td>33.30±0.90</td>
<td>2012 Calc.(^1)</td>
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<td>31.72</td>
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### Table XLVIII. Molar entropy (cal K\(^{-1}\) mol\(^{-1}\)) of 2-methylallyl radical.

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<tr>
<td>3(^{rd})Millennium(^3)</td>
<td>71.79</td>
<td>2012</td>
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<tr>
<td>Goldsmith \textit{et al.}(^4)</td>
<td>70.20±1.30</td>
<td>2012 Calc.*</td>
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<tr>
<td><strong>Recommendation</strong></td>
<td><strong>71.05</strong></td>
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<td><strong>GA</strong></td>
<td>70.57</td>
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### Table XLIX. Enthalpy of formation (kcal mol\(^{-1}\)) of 1-methylallyl radical.

<table>
<thead>
<tr>
<th>Literature</th>
<th>(\Delta_f H^\circ)</th>
<th>Year</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>McMillen and Golden(^6)</td>
<td>30.40</td>
<td>1982</td>
<td>Rev.</td>
</tr>
<tr>
<td>Traeger(^5)</td>
<td>35.30</td>
<td>1989</td>
<td>Exp*</td>
</tr>
<tr>
<td>Baulch \textit{et al.}(^3)</td>
<td>33.40</td>
<td>2005</td>
<td>Rev.</td>
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<tr>
<td>Lau \textit{et al.}(^7)</td>
<td>33.10±0.96</td>
<td>2007 Calc.(^*)</td>
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<tr>
<td>Agapito \textit{et al.}(^8)</td>
<td>33.94±0.96</td>
<td>2007 Calc.(^*)</td>
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<td>3(^{rd})Millennium(^3)</td>
<td>32.53</td>
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<tr>
<td>Goldsmith \textit{et al.}(^4)</td>
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<td><strong>GA</strong></td>
<td>33.09</td>
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\(^*\) PI \quad \(^*\)\(^*\) CCSD(T)/CBS \quad \(^1\) QCISDT
The average molar entropy of 1-methylallyl radical is 71.35 cal K\(^{-1}\) mol\(^{-1}\) with a standard deviation of 1.80 cal K\(^{-1}\) mol\(^{-1}\). All of the values in Tables L agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is 70.91 cal K\(^{-1}\) mol\(^{-1}\).

C. Alcohols and related radicals

1. Ethanol

The studies that report values for the heat of formation for ethanol are included in Table LI, while those that report molar entropy values are included in Table LII.

The average heat of formation for ethanol is -56.10 kcal mol\(^{-1}\) with a standard deviation of 0.12 kcal mol\(^{-1}\). All of the values in Table LI agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is -56.13 kcal mol\(^{-1}\).

2. Ethoxy radical

There are several studies that proposed values for the heat of formation of the ethoxy radical which are in the range -6.00 to -1.70 kcal mol\(^{-1}\) as shown in Table LIII. The limited studies that report values for the molar entropy are in better agreement and range from 65.60 to 66.80 cal K\(^{-1}\) mol\(^{-1}\), Table LIV.

The average heat of formation of the ethoxy radical is -3.24 kcal mol\(^{-1}\) with a standard deviation of 1.01 kcal.
that value is excluded the average becomes which is more than twice the standard deviation. When
for the molar entropy is limited.

<table>
<thead>
<tr>
<th>Literature</th>
<th>𝑆^∗</th>
<th>Year</th>
<th>Source</th>
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<td>Rauk et al.(^\ddagger)</td>
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<td>Baulch et al.(^\ddagger)</td>
<td>65.60</td>
<td>2005</td>
<td>Rev.</td>
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<td>Rusic et al.(^\ddagger)</td>
<td>66.36±0.96</td>
<td>2005</td>
<td>Rev.</td>
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<td>3(^\text{rd})Millennium(^\ddagger)</td>
<td>65.15</td>
<td>2012</td>
<td></td>
</tr>
<tr>
<td>Goldsmith et al.(^\ddagger)</td>
<td>66.80±1.0</td>
<td>2012</td>
<td>Calc.**</td>
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<td><strong>Standard Deviation</strong></td>
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<td><strong>Recommendation</strong></td>
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<td><strong>GA</strong></td>
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\(^\ddagger\) CBS-Q and B3LYP
\(^\ddagger\) QCISDT

TABLE L VI. Molar entropy (cal K\(^{-1}\) mol\(^{-1}\)) of ethoxy radical.

\(\Delta_f H\) of ethoxy radical is \(-13.39\) kcal mol\(^{-1}\) with a standard deviation of \(0.85\) kcal mol\(^{-1}\). The recommendation from Baulch et al.\(^\ddagger\) differs from the average by \(1.85\) kcal mol\(^{-1}\) which is more than twice the standard deviation. When this value is excluded the average becomes \(-13.65\) kcal mol\(^{-1}\). The value estimated using group additivity after optimisation is \(-13.15\) kcal mol\(^{-1}\).

The average molar entropy for 1-hydroxy ethyl radical is \(68.09\) cal K\(^{-1}\) mol\(^{-1}\) with a standard deviation of \(0.80\) cal K\(^{-1}\) mol\(^{-1}\). The three values in Table LVI agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is \(67.89\) cal K\(^{-1}\) mol\(^{-1}\).

4. 2-Hydroxy ethyl radical

2-hydroxy ethyl radical is the ethanol radical where the radical is located on the carbon β to the hydroxyl group. While there are several studies that report heat of formation values (Table LVII), very few studies report values for the standard molar entropy of the 2-hydroxy ethyl radical (Table LVIII).

The average of heat of formation for the 2-hydroxy ethyl radical is \(-7.46\) kcal mol\(^{-1}\) with a standard deviation of \(2.23\) kcal mol\(^{-1}\). The measured value from Holmes\(^\ddagger\) differs from the average by \(\approx 6\) kcal mol\(^{-1}\) which is more than twice the standard deviation. When that value is excluded the average becomes \(-6.91\) kcal mol\(^{-1}\). The value estimated using group additivity after optimisation is \(-6.45\) kcal mol\(^{-1}\).

The average molar entropy for 2-hydroxy ethyl radical is \(69.21\) cal K\(^{-1}\) mol\(^{-1}\) with a standard deviation of \(1.65\) cal K\(^{-1}\) mol\(^{-1}\). The three values in Table LVIII agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is \(70.14\) cal K\(^{-1}\) mol\(^{-1}\).

5. n-Propanol

There is good agreement within the literature for the heat of formation for n-propanol values as shown in Ta-
Table LVI. Enthalpy of formation (kcal mol$^{-1}$) of 2-hydroxy ethyl radical.

Table LX. Molar entropy (cal K$^{-1}$ mol$^{-1}$) of propanol.

Table LXI. Enthalpy of formation (kcal mol$^{-1}$) of $n$-propoxy radical.

Table LXII. Molar entropy (cal K$^{-1}$ mol$^{-1}$) of $n$-propoxy radical.

Table LXIII. Enthalpy of formation (kcal mol$^{-1}$) of propanol.

Table LXIV. Molar entropy (cal K$^{-1}$ mol$^{-1}$) of propanol.

Table LXV. Molar entropy (cal K$^{-1}$ mol$^{-1}$) of propanol.

Table LXVI. Molar entropy (cal K$^{-1}$ mol$^{-1}$) of propanol.

Table LXVII. Molar entropy (cal K$^{-1}$ mol$^{-1}$) of propanol.

Table LXVIII. Molar entropy (cal K$^{-1}$ mol$^{-1}$) of propanol.

Table LXIX. Molar entropy (cal K$^{-1}$ mol$^{-1}$) of propanol.

Table LX. Molar entropy (cal K$^{-1}$ mol$^{-1}$) of propanol.

Table LXI. Enthalpy of formation (kcal mol$^{-1}$) of $n$-propoxy radical.

Table LXII. Molar entropy (cal K$^{-1}$ mol$^{-1}$) of $n$-propoxy radical.

Table LXIII. Enthalpy of formation (kcal mol$^{-1}$) of propanol.

Table LXIV. Molar entropy (cal K$^{-1}$ mol$^{-1}$) of propanol.

Table LXV. Molar entropy (cal K$^{-1}$ mol$^{-1}$) of propanol.

Table LXVI. Molar entropy (cal K$^{-1}$ mol$^{-1}$) of propanol.

Table LXVII. Molar entropy (cal K$^{-1}$ mol$^{-1}$) of propanol.
 TABLE LXIII. Enthalpy of formation (kcal mol\(^{-1}\)) of iso-propanol.

<table>
<thead>
<tr>
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<th>Source</th>
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<tr>
<td>Parks et al.(^{54})</td>
<td>–65.20</td>
<td>1950</td>
<td>Exp(^*)</td>
</tr>
<tr>
<td>Snelson and Skinner(^{95})</td>
<td>–65.07</td>
<td>1965</td>
<td>Exp(^*)</td>
</tr>
<tr>
<td>Buckley and Herington(^{98})</td>
<td>–65.20</td>
<td>1965</td>
<td>Exp(^*)</td>
</tr>
<tr>
<td>Lange’s Handbook(^1)</td>
<td>–56.12</td>
<td>1999</td>
<td>Rev.</td>
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<tr>
<td>Sun and Bozzelli(^{99})</td>
<td>–65.19 (\pm) 0.31</td>
<td>2002</td>
<td>Calc.(^1)</td>
</tr>
<tr>
<td>3(^{rd}) Millennium(^3)</td>
<td>–65.18</td>
<td>2012</td>
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<tr>
<td>Goldsmith et al.(^4)</td>
<td>–65.40 (\pm) 0.30</td>
<td>2012</td>
<td>Calc.(^1)</td>
</tr>
<tr>
<td>ATcF(^2)</td>
<td>–65.20 (\pm) 0.09</td>
<td>2012</td>
<td>Calc.(^5)</td>
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<tr>
<td>Verenkin(^5)</td>
<td>–64.91</td>
<td>2013</td>
<td>Rev.</td>
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* Standard Deviation 0.13

** Recommendation – 65.16

GA – 65.16

\(^*\) CALORIMETRY \(^**\) KINETICS
\(^\dagger\) CBSQ//B3 \(^\ddagger\) QCISDT
\(^\S\) TN

TABLE LXIV. Molar entropy (cal K\(^{-1}\) mol\(^{-1}\)) of iso-propanol.

<table>
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<th>Literature</th>
<th>(S^\circ)</th>
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<th>Source</th>
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<td>Lange’s Handbook(^\S)</td>
<td>73.90</td>
<td>1999</td>
<td>Rev.</td>
</tr>
<tr>
<td>Sun and Bozzelli(^{99})</td>
<td>72.89</td>
<td>2002</td>
<td>Calc.(^*)</td>
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<tr>
<td>3(^{rd}) Millennium(^3)</td>
<td>73.91</td>
<td>2012</td>
<td></td>
</tr>
<tr>
<td>Goldsmith et al.(^4)</td>
<td>73.90 (\pm) 1.60</td>
<td>2012</td>
<td>Calc.(^*)</td>
</tr>
</tbody>
</table>

* Standard Deviation 0.50

** Recommendation 73.73

GA 73.73

\(^*\) CBSQ//B3 \(^**\) QCISDT

8. iso-Propanol

There is good agreement within the literature for both the heat of formation and molar entropy of iso-propanol as shown in Tables LXIII and LXIV.

The average heat of formation for iso-propanol is –65.16 kcal mol\(^{-1}\) with a standard deviation of 0.13 kcal mol\(^{-1}\). All of the values in Table LXIII agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is –65.16 kcal mol\(^{-1}\).

The average molar entropy for iso-propanol is 73.73 cal K\(^{-1}\) mol\(^{-1}\) with a standard deviation of 0.50 cal K\(^{-1}\) mol\(^{-1}\). All of the values in Table LXIV agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is 73.73 cal K\(^{-1}\) mol\(^{-1}\).

TABLE LXVI. Molar entropy (cal K\(^{-1}\) mol\(^{-1}\)) of iso-propanoxy radical.

<table>
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<th>Literature</th>
<th>(S^\circ)</th>
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<th>Source</th>
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<tr>
<td>Sun and Bozzelli(^{99})</td>
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<td>Rauk et al.(^{11})</td>
<td>72.99</td>
<td>2003</td>
<td>Calc.(^*)</td>
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<td>Goldsmith et al.(^4)</td>
<td>72.16 (\pm) 1.50</td>
<td>2012</td>
<td>Calc.(^\dagger)</td>
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* Standard Deviation 0.86

** Recommendation 72.16

GA 72.02

\(^*\) CBSQ//B3 \(^**\) CBS-RAD \(^\dagger\) QCISDT
Within twice the standard deviation. The value estimated using group additivity after optimisation is 72.02 cal K\(^{-1}\) mol\(^{-1}\). The three values in Table LXVI agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is 72.02 cal K\(^{-1}\) mol\(^{-1}\).

D. Aldehydes and ketones

While there are numerous studies that report thermo-

dynamic values for aldehydes and ketones, there are very few studies that report data for the related radicals. To this end only the thermochemical data for the stable species are reported herein. Further study of these radicals is recommended.

1. Ethanal/acetaldehyde

There are several studies that recommend heat of for-
mation and molar entropy values for ethanal as shown in
Tables LXVII and LXVIII below.

The average heat of formation for ethanal is

\(-39.65\) kcal mol\(^{-1}\) with a standard deviation of 0.39 kcal mol\(^{-1}\). All of these values in Table LXVII agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is \(-39.65\) kcal mol\(^{-1}\).

The average molar entropy of ethanal is 63.02 cal K\(^{-1}\) mol\(^{-1}\) with a standard deviation of 0.58 kcal mol\(^{-1}\). All of the values in Table LXVIII agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is 63.07 cal K\(^{-1}\) mol\(^{-1}\).

2. Propanal

The studies that recommend heat of formation and

molar entropy values for propanal are included in Ta-

bles LXIX and LXX below.

<table>
<thead>
<tr>
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<td>Chao et al.(^{29})</td>
<td>(-39.72)</td>
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<td>Wiberg et al.(^{100})</td>
<td>(-47.80)</td>
<td>1991</td>
<td>Exp**</td>
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<tr>
<td>da Silva and Bozze</td>
<td>(-39.72)</td>
<td>2006</td>
<td>Calc.†</td>
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<td>3rd Millennium(^{3})</td>
<td>(-39.72)</td>
<td>2012</td>
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<td>Verevkin et al.(^{5})</td>
<td>(-39.51)</td>
<td>2013</td>
<td>Rev.</td>
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<td>Goldsmith et al.(^{4})</td>
<td>(-39.60 \pm 0.10)</td>
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<td>Calc.†</td>
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<td><strong>Standard Deviation</strong></td>
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<td><strong>Recommendation</strong></td>
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<tr>
<td><strong>GA</strong></td>
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</table>

\(^{*}\) RRHO  \(^{**}\) KINETICS  \(^{†}\) QCISDT

TABLE LXVII. Enthalpy of formation (kcal mol\(^{-1}\)) of ethanal.

The average heat of formation for propanal is \(-45.07\) kcal mol\(^{-1}\) with a standard deviation of 0.58 kcal mol\(^{-1}\). All of the values in Table LXIX agree with the average within twice the standard deviation. The heat of formation values using group additivity after optimisation is \(-44.76\) kcal mol\(^{-1}\).

The average molar entropy of propanal is 72.01 cal K\(^{-1}\) mol\(^{-1}\) with a standard deviation of 0.05 cal K\(^{-1}\) mol\(^{-1}\). All of the values in Table LXX agree with the average within twice the standard deviation. The value estimated

<table>
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<th>Literature</th>
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<tr>
<td>Lange's Handbook(^{21})</td>
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<tr>
<td>Lee and Bozze</td>
<td>63.13</td>
<td>2006</td>
<td>Calc.*</td>
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<tr>
<td>CRC(^{22})</td>
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<td>3rd Millennium(^{3})</td>
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<td>Goldsmith et al.(^{4})</td>
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<td>Calc.**</td>
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<td><strong>Standard Deviation</strong></td>
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\(^{*}\) CBSQ  \(^{**}\) QCISDT

TABLE LXVIII. Molar entropy (cal K\(^{-1}\) mol\(^{-1}\)) of ethanal.

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<th>Source</th>
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<td>Tjebbes(^{103})</td>
<td>(-45.76)</td>
<td>1986</td>
<td>Calc.*</td>
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<tr>
<td>Buckey and Cox(^{104})</td>
<td>(-45.90)</td>
<td>1986</td>
<td>Exp**</td>
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<td>Connett(^{24})</td>
<td>(-44.46)</td>
<td>1972</td>
<td>Exp**</td>
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<tr>
<td>Wiberg et al.(^{100})</td>
<td>(-45.09)</td>
<td>1991</td>
<td>Exp**</td>
</tr>
<tr>
<td>Lange's Handbook(^{21})</td>
<td>(-44.36)</td>
<td>1999</td>
<td>Rev.</td>
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<tr>
<td>da Silva and Bozze</td>
<td>(-45.18)</td>
<td>2006</td>
<td>Calc.†</td>
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<td>3rd Millennium(^{3})</td>
<td>(-44.25)</td>
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<tr>
<td>Verevkin et al.(^{5})</td>
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<tr>
<td>Goldsmith et al.(^{4})</td>
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<td>2012</td>
<td>Calc.†</td>
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<tr>
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<tr>
<td><strong>Recommendation</strong></td>
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<tr>
<td><strong>GA</strong></td>
<td>(-44.76)</td>
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\(^{*}\) RRHO  \(^{**}\) KINETICS  \(^{†}\) QCISDT

TABLE LXIX. Enthalpy of formation (kcal mol\(^{-1}\)) of propanal.

<table>
<thead>
<tr>
<th>Literature</th>
<th>(S^\circ)</th>
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<td>Connett(^{94})</td>
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<td>Lange's Handbook(^{21})</td>
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<td>1999</td>
<td>Rev.</td>
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<tr>
<td>3rd Millennium(^{3})</td>
<td>69.03</td>
<td>2012</td>
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<tr>
<td>Goldsmith et al.(^{4})</td>
<td>73.50 ±1.3</td>
<td>2012</td>
<td>Calc.**</td>
</tr>
<tr>
<td><strong>Standard Deviation</strong></td>
<td>1.75</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Recommendation</strong></td>
<td>72.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>GA</strong></td>
<td>71.58</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{*}\) KINETICS  \(^{**}\) QCISDT

TABLE LXX. Molar entropy of formation (cal K\(^{-1}\) mol\(^{-1}\)) of propanal.
Table LXXI. Enthalpy of formation (kcal mol\(^{-1}\)) of butanal.

<table>
<thead>
<tr>
<th>Literature</th>
<th>(\Delta_f H^0)</th>
<th>Year</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tjebbes(^{103})</td>
<td>(-49.02)</td>
<td>1986</td>
<td>Calc.(^*)</td>
</tr>
<tr>
<td>Buckley and Cox(^{104})</td>
<td>(-48.85)</td>
<td>1986</td>
<td>Exp.(^**)</td>
</tr>
<tr>
<td>Connet(^{24})</td>
<td>(-44.46)</td>
<td>1972</td>
<td>Exp.(^**)</td>
</tr>
<tr>
<td>Wiberg et al.(^{100})</td>
<td>(-50.61)</td>
<td>1991</td>
<td>Exp.(^**)</td>
</tr>
<tr>
<td>da Silva and Bovelli(^{101})</td>
<td>(-49.27)</td>
<td>2006</td>
<td>Calc.(^\dagger)</td>
</tr>
<tr>
<td>3rd Millennium(^3)</td>
<td>(-49.27)</td>
<td>2012</td>
<td>Rev.</td>
</tr>
<tr>
<td>Verevkin et al.(^{5})</td>
<td>(-50.72)</td>
<td>2013</td>
<td>Rev.</td>
</tr>
</tbody>
</table>

**Standard Deviation 0.67**

**Recommendation 80.45**

**GA** | \(-49.76\)

**RRHO**

**G3, G3B3, & CBS-APNO**

**QCISDT**

Table LXXII. Molar entropy (cal K\(^{-1}\) mol\(^{-1}\)) of butanal.

<table>
<thead>
<tr>
<th>Literature</th>
<th>(S^\circ)</th>
<th>Year</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lange’s Handbook(^{21})</td>
<td>82.15</td>
<td>1999 Rev.</td>
<td></td>
</tr>
<tr>
<td>3rd Millennium(^3)</td>
<td>78.24</td>
<td>2012</td>
<td></td>
</tr>
<tr>
<td>Seal et al.(^{105})</td>
<td>82.00</td>
<td>2012 Calc.(^*)</td>
<td></td>
</tr>
</tbody>
</table>

**Standard Deviation 1.96**

**Recommendation 80.80**

**GA** | 81.23 |

Calorimetry

**KINETICS**

**QCISDT**

3. Butanal

The studies that recommend heat of formation and molar entropy values for butanal are included in Tables LXXI and LXXII below.

The average heat of formation of butanal is \(-49.45\) kcal mol\(^{-1}\) with a standard deviation of 0.67 kcal mol\(^{-1}\). All of the values in Table LXXI agree with the average within twice the standard deviation. The heat of formation values using group additivity after optimisation is \(-49.76\) kcal mol\(^{-1}\).

The average molar entropy of butanal is 80.80 cal K\(^{-1}\) mol\(^{-1}\) with a standard deviation of 1.96 cal K\(^{-1}\) mol\(^{-1}\). The three values in Table LXXII agree with the average within twice the standard deviation. The molar entropy estimated using group additivity after optimisation is 81.23 cal K\(^{-1}\) mol\(^{-1}\).

4. Propanone/acetone

There are several studies that recommend heat of formation and molar entropy values for acetone as shown in Tables LXXIII and LXXIV below.

<table>
<thead>
<tr>
<th>Literature</th>
<th>(\Delta_f H^0)</th>
<th>Year</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pennington and Kobe(^{106})</td>
<td>70.49</td>
<td>1957 Exp(^*)</td>
<td></td>
</tr>
<tr>
<td>Buckley and Herington(^98)</td>
<td>70.04</td>
<td>1965 Exp.(^**)</td>
<td></td>
</tr>
<tr>
<td>Chao and Zvolinski(^{107})</td>
<td>70.59</td>
<td>1976 Rev.</td>
<td></td>
</tr>
<tr>
<td>Chao et al.(^{59})</td>
<td>71.13</td>
<td>1976 Rev.</td>
<td></td>
</tr>
<tr>
<td>Lange’s Handbook(^{21})</td>
<td>70.57</td>
<td>1999 Rev.</td>
<td></td>
</tr>
<tr>
<td>Janoschek and Rossi(^{109})</td>
<td>70.66</td>
<td>2004 Calc.(^\dagger)</td>
<td></td>
</tr>
<tr>
<td>Sander et al.(^{111})</td>
<td>70.61</td>
<td>2011 Rev.</td>
<td></td>
</tr>
<tr>
<td>3rd Millennium(^3)</td>
<td>70.66</td>
<td>2012</td>
<td></td>
</tr>
<tr>
<td>Goldsmith et al.(^4)</td>
<td>70.90 (\pm)0.90</td>
<td>2012 Calc.(^\dagger)</td>
<td></td>
</tr>
<tr>
<td>Verevkin et al.(^{5})</td>
<td>70.57</td>
<td>2013 Rev.</td>
<td></td>
</tr>
</tbody>
</table>

**Standard Deviation 0.23**

**Recommendation 70.63**

**GA** | 71.00 |

Calorimetry

**KINETICS**

**QCISDT**

There is also good agreement among the literature heat of formation values in Table LXXIII for acetone. The average is \(-51.86\) kcal mol\(^{-1}\) with a standard deviation of 0.22 kcal mol\(^{-1}\). The recommendation in the 3rd Millennium database differs from the average by 0.52 kcal mol\(^{-1}\) which is more than twice the standard deviation. When this value is excluded the average becomes \(-51.91\) kcal mol\(^{-1}\). The heat of formation values estimated using group additivity after optimisation is \(-52.12\) kcal mol\(^{-1}\).

There is also good agreement among the literature molar entropy values in Table LXXIV for acetone. The average molar entropy is 70.56 cal K\(^{-1}\) mol\(^{-1}\) with a standard deviation of 0.23 cal K\(^{-1}\) mol\(^{-1}\). The recommendation
than twice the standard deviation and when this value is from the 1965 study by Buckley and Herington\(^{98}\)
from the average by 0.52 cal K\(^{-1}\) mol\(^{-1}\) which is more than twice the standard deviation and when this value is excluded the average becomes 70.63 cal K\(^{-1}\) mol\(^{-1}\). The molar entropy value estimated using group additivity after optimisation is 71.00 cal K\(^{-1}\) mol\(^{-1}\).

5. Butanone

There are several studies that recommend heat of formation and molar entropy values for butanone as shown in Tables LXXV and LXXVI below.

![Butanone structure](image)

There are fewer values available for butanone in comparison to acetone however, there is good agreement among the literature heat of formation values in Table LXXV. The average is \(-57.10\) kcal mol\(^{-1}\) with a standard deviation of 0.14 kcal mol\(^{-1}\). All of the values in Table LXXV agree with the average within twice the standard deviation. The heat of formation value estimated using group additivity after optimisation is \(-57.23\) kcal mol\(^{-1}\).

There are few values available in the literature for the molar entropy of butanone. The 3\(^{rd}\) Millennium database recommends a value of 81.27 cal K\(^{-1}\) mol\(^{-1}\) while Lange’s handbook recommends 81.24 cal K\(^{-1}\) mol\(^{-1}\). The molar entropy value estimated using group additivity after optimisation is 80.88 cal K\(^{-1}\) mol\(^{-1}\), which differs from the average by 0.37 cal K\(^{-1}\) mol\(^{-1}\). Further study of the molar entropy of butanone is recommended.

### Ethyl hydroperoxide

Several studies report values for the heat of formation for ethyl hydroperoxide (Table LXXVII), however recommendations for the standard molar entropy are limited (Table LXXVIII).

The average heat of formation of ethyl hydroperoxide is \(-40.47\) kcal mol\(^{-1}\) with a standard deviation of 2.83 kcal mol\(^{-1}\). The experimental recommendation from the 1940 study by Stathis and Egerton\(^{113}\) differs from the average by 7.33 kcal mol\(^{-1}\) which is more than twice the standard deviation. When this value is excluded the average becomes \(-39.81\) kcal mol\(^{-1}\). The value estimated using group additivity after optimisation is \(-38.63\) kcal mol\(^{-1}\).

The average molar entropy of ethyl hydroperoxide is 75.59 cal K\(^{-1}\) mol\(^{-1}\) with a standard deviation of 0.46 cal K\(^{-1}\) mol\(^{-1}\). The three values included in Table LXXVIII...
agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is \(74.74 \text{ cal K}^{-1} \text{ mol}^{-1}\).

2. Ethyl peroxy radical

There are a number of studies that report values for the heat of formation of the ethyl peroxy radical in the literature and they show relatively good agreement as shown in Table LXXIX. Table LXXX shows that there are fewer values for the molar entropy but there is good agreement among the limited values.

The average heat of formation for the ethyl peroxy radical is \(-5.71 \text{ kcal mol}^{-1}\) with a standard deviation of 1.34 kcal mol\(^{-1}\). The calculated value reported by Shallcross et al.\(^{123}\) differs from the average by 3.42 kcal mol\(^{-1}\) which is more than twice the standard deviation. When this value is excluded the average becomes \(-6.09 \text{ kcal mol}^{-1}\). The value estimated using group additivity after optimisation is \(-5.46 \text{ kcal mol}^{-1}\).

The average molar entropy for the ethyl peroxy radical is 73.95 cal K\(^{-1}\) mol\(^{-1}\) with a standard deviation of 0.23 cal K\(^{-1}\) mol\(^{-1}\). All of the values in Table LXXX agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is 74.26 cal K\(^{-1}\) mol\(^{-1}\).

3. \(n\)-Propyl hydroperoxide

There is relatively good agreement in the literature of the heat of formation of \(n\)-propyl hydroperoxide as shown in Table LXXXI. As with ethyl peroxy radical there are few values for the standard molar entropy for \(n\)-propyl hydroperoxide available in the literature (Table LXXXII).

The average heat of formation of \(n\)-propyl hydroperoxide is \(-46.56 \text{ kcal mol}^{-1}\) with a standard deviation of 5.58 kcal mol\(^{-1}\). The experimental recommendation from the 1940 study by Stathis and Egerton\(^{113}\) differs from the average by 13.44 kcal mol\(^{-1}\) which is more than twice the standard deviation. When this value is excluded the average becomes \(-43.87 \text{ kcal mol}^{-1}\). The value estimated using group additivity after optimisation is \(-43.63 \text{ kcal mol}^{-1}\).

The average molar entropy for \(n\)-propyl hydroperox-
5. iso-Propyl hydroperoxide

The value estimated using group additivity after optimisation is 80.98 ± 0.90 2012 Calc.†

** CBS-QB3 † QCISDT

TABLE LXXXIII. Enthalpy of formation (kcal mol⁻¹) of n-propyl peroxy radical.

<table>
<thead>
<tr>
<th>Literature</th>
<th>Δ_fH°</th>
<th>Year Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Villano et al.¹²⁴</td>
<td>-10.42</td>
<td>2011 Calc.†</td>
</tr>
<tr>
<td>3rd Millennium³</td>
<td>-10.15</td>
<td>2012</td>
</tr>
<tr>
<td>Goldsmith et al.¹⁴</td>
<td>-0.80 ±0.90 2012 Calc.†</td>
<td></td>
</tr>
</tbody>
</table>

Standard Deviation 0.45

Recommendation -10.42

GA -10.46

** CBS-QB3 † QCISDT

4. n-Propyl peroxy radical

There are only a limited number of studies that report values for both the heat of formation and molar entropy of the n-propyl peroxy radical as shown in Tables LXXXIII and LXXXIV.

The average heat of formation for the n-propyl peroxy radical is -10.42 kcal mol⁻¹ with a standard deviation of 0.45 kcal mol⁻¹. All of the values in Table LXXXII agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is -10.46 kcal mol⁻¹.

The average molar entropy for the n-propyl peroxy radical is 81.31 cal K⁻¹ mol⁻¹ with a standard deviation of 2.61 cal K⁻¹ mol⁻¹. The three values in Table LXXXIV agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is 83.91 cal K⁻¹ mol⁻¹.

5. iso-Propyl hydroperoxide

The values for the heat of formation iso-propyl hydroperoxide range from -51.00 kcal mol⁻¹ to -46.50 kcal mol⁻¹ and are shown in Table LXXXV, there are fewer values available for the molar entropy as shown in Table LXXXVI.

The average heat of formation for the iso-propyl hydroperoxide is 48.36 kcal mol⁻¹ with a standard deviation of 1.39 kcal mol⁻¹. All of the values in Table LXXXV agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is -47.65 kcal mol⁻¹.

The average molar entropy for the iso-propyl hydroperoxide is 81.19 cal K⁻¹ mol⁻¹ with a standard deviation of 0.99 cal K⁻¹ mol⁻¹. All of the values in Table LXXXVI agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is 80.76 cal K⁻¹ mol⁻¹.

6. iso-Propyl peroxy radical

While there are several studies that report values for the heat of formation for the iso-propyl peroxy radical as shown in Table LXXXVII, as far as the author of this study is aware there are only two studies that reported values for the standard molar entropy (Table LXXXVII).

The average heat of formation for the iso-propyl peroxy radical is -14.33 kcal mol⁻¹ with a standard deviation of 2.38 kcal mol⁻¹. The value from Shallcross et al.¹²³ differs from the average by 5.54 kcal mol⁻¹ which

TABLE LXXXIV. Molar entropy (cal K⁻¹ mol⁻¹) of n-propyl peroxy radical.

<table>
<thead>
<tr>
<th>Literature</th>
<th>S°</th>
<th>Year Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Villano et al.¹²⁴</td>
<td>82.80</td>
<td>2011 Calc.†</td>
</tr>
<tr>
<td>3rd Millennium³</td>
<td>77.64</td>
<td>2012</td>
</tr>
<tr>
<td>Goldsmith et al.¹⁴</td>
<td>83.50 ±1.90 2012 Calc.**</td>
<td></td>
</tr>
</tbody>
</table>

Standard Deviation 2.61

Recommendation 81.31

GA 83.91

** CBS-QB3 † QCISDT

TABLE LXXXV. Enthalpy of formation (kcal mol⁻¹) of iso-propyl hydroperoxide.

<table>
<thead>
<tr>
<th>Literature</th>
<th>Δ_fH°</th>
<th>Year Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Knyazev⁹⁵</td>
<td>-51.00</td>
<td>1998 Exp †</td>
</tr>
<tr>
<td>Chen et al.¹¹⁵</td>
<td>-48.99±0.32 2000 Calc.**</td>
<td></td>
</tr>
<tr>
<td>Sumathi and Green¹²⁵</td>
<td>-48.05</td>
<td>2003 Calc.**</td>
</tr>
<tr>
<td>Janoschek et al.¹⁰⁹</td>
<td>-46.50</td>
<td>2003 Calc.†</td>
</tr>
<tr>
<td>Simmie et al.¹²⁰</td>
<td>-47.90</td>
<td>2008 Calc.**</td>
</tr>
<tr>
<td>Goldsmith et al.¹⁴</td>
<td>-47.70 ±0.90 2012 Calc.‡</td>
<td></td>
</tr>
</tbody>
</table>

Standard Deviation 1.39

Recommendation -48.36

GA -47.65

† G3MP2B3 ‡ QCISDT

TABLE LXXXV. Enthalpy of formation (kcal mol⁻¹) of iso-propyl hydroperoxide.
8. n-Butyl peroxo radical

Values for the heat of formation for the n-butyl hydroperoxo radical are in the range of $-17.14$ kcal mol$^{-1}$ (Zhu et al.$^{126}$) to $-15.00$ kcal mol$^{-1}$ (Simmie et al.$^{120}$).

The average heat of formation value for the n-butyl peroxy radical is $-15.70$ kcal mol$^{-1}$ with a standard deviation of $0.85$ kcal mol$^{-1}$. All of the literature values in Table XCI agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is $-15.46$ kcal mol$^{-1}$.

The average molar entropy value for the n-butyl peroxy radical is $92.39$ cal K$^{-1}$ mol$^{-1}$ with a standard deviation of $0.96$ cal K$^{-1}$ mol$^{-1}$. The three literature values in Table XCI agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is $93.56$ cal K$^{-1}$ mol$^{-1}$.

<table>
<thead>
<tr>
<th>Literature</th>
<th>$\Delta_f H^\circ$</th>
<th>Year Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zhu et al.$^{126}$</td>
<td>$-49.74$</td>
<td>2007 Calc.*</td>
</tr>
<tr>
<td>Simmie et al.$^{120}$</td>
<td>$-48.37$</td>
<td>2011 Calc.**</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>$0.69$</td>
<td></td>
</tr>
<tr>
<td>Recommendation</td>
<td>$-49.06$</td>
<td></td>
</tr>
<tr>
<td>GA</td>
<td>$-48.63$</td>
<td></td>
</tr>
</tbody>
</table>

* CBS-QB  ** PM3

TABLE LXXXIX. Enthalpy of formation (kcal mol$^{-1}$) of n-butyl hydroperoxide.

<table>
<thead>
<tr>
<th>Literature</th>
<th>$\Delta_f H^\circ$</th>
<th>Year Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zhu et al.$^{126}$</td>
<td>$-17.14$</td>
<td>2007 Calc.*</td>
</tr>
<tr>
<td>Simmie et al.$^{120}$</td>
<td>$-15.00$</td>
<td>2011 Calc.**</td>
</tr>
<tr>
<td>Villano et al.$^{124}$</td>
<td>$-15.46$</td>
<td>2011 Calc.*</td>
</tr>
<tr>
<td>$3^{rd}$ Millennium$^3$</td>
<td>$-15.18$</td>
<td>2012</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>$0.85$</td>
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</tr>
<tr>
<td>Recommendation</td>
<td>$-15.70$</td>
<td></td>
</tr>
<tr>
<td>GA</td>
<td>$-15.46$</td>
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</tbody>
</table>

* CBS-QB  ** PM3

TABLE XC. Enthalpy of formation (kcal mol$^{-1}$) of n-butyl peroxy radical.

7. n-Butyl hydroperoxide

The literature data for both heats of formation and molar entropy for n-butyl hydroperoxide are limited.

The average of the two heat of formation values is $-49.06$ kcal mol$^{-1}$ with a standard deviation of $0.69$ kcal mol$^{-1}$. The value estimated using group additivity after optimisation is $-48.63$ kcal mol$^{-1}$.

The Zhu et al.$^{126}$ study also reported a value of $92.82$ cal K$^{-1}$ mol$^{-1}$ for the standard molar entropy, while the value estimated using group additivity after optimisation is $94.04$ cal K$^{-1}$ mol$^{-1}$. Further studies are required to acquire a more accurate estimate of the uncertainty for the heat of formation and molar entropy of n-butyl hydroperoxide.

<table>
<thead>
<tr>
<th>Literature</th>
<th>$S^\circ$</th>
<th>Year Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zhu et al.$^{126}$</td>
<td>$93.55$</td>
<td>2007 Calc.*</td>
</tr>
<tr>
<td>Villano et al.$^{124}$</td>
<td>$92.43$</td>
<td>2011 Calc.*</td>
</tr>
<tr>
<td>$3^{rd}$ Millennium$^3$</td>
<td>$91.19$</td>
<td>2012</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>$0.96$</td>
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<td>Recommendation</td>
<td>$92.39$</td>
<td></td>
</tr>
<tr>
<td>GA</td>
<td>$93.56$</td>
<td></td>
</tr>
</tbody>
</table>

* CBS-QB

TABLE XCI. Molar entropy (cal K$^{-1}$ mol$^{-1}$) of n-butyl peroxy radical.
III. ALCOHOLIC HYDROPEROXIDES

A. Comparison of thermochemical data from the literature and group additivity

Table XCI compares the thermochemical properties calculated using the new group values and the values calculated theoretically for alcoholic hydroperoxides an example is shown in Fig. 2. Some of the theoretical calculations were shared via private communications\textsuperscript{127,128}.

\[
\begin{array}{c}
\text{OH} \\
\text{H}_3\text{C} - \text{CH} \\
\text{O} - \text{OH}
\end{array}
\]

FIG. 2. Example of alcoholic hydroperoxide, CH\textsubscript{3}CHOOH(OH).
TABLE XCII. THERM predictions of thermodynamic properties compared to calculated values for alcoholic hydroperoxide species.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Source</th>
<th>( \Delta H^\circ ) kcal mol(^{-1})</th>
<th>( \Delta S^\circ ) cal mol(^{-1}) K(^{-1})</th>
<th>( C_p ) cal mol(^{-1}) K(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH(_3)CHOOH(OH)</td>
<td>GA(^{127*})</td>
<td>-85.49</td>
<td>80.48</td>
<td>24.48</td>
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<tr>
<td></td>
<td></td>
<td>-85.61</td>
<td>78.18</td>
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</tr>
<tr>
<td>CH(_3)CHOO*(OH)</td>
<td>GA(^{127*})</td>
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</tr>
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<td>-50.62</td>
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<td></td>
</tr>
<tr>
<td>CH(_3)CH(_2)CHOOH(OH)</td>
<td>GA(^{127*})</td>
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<tr>
<td></td>
<td></td>
<td>-90.48</td>
<td>90.22</td>
<td>29.97</td>
</tr>
<tr>
<td>CH(_3)CH(_2)CHOO*(OH)</td>
<td>GA(^{127*})</td>
<td>-55.79</td>
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<td>28.00</td>
</tr>
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<td></td>
<td></td>
<td>-55.75</td>
<td>90.13</td>
<td>27.78</td>
</tr>
</tbody>
</table>

* CBS-QB3
** G3B3
† B3LYP/CBSB7
### Table 1: Molar enthalpy of formation for various molecules

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Ref</th>
<th>C&lt;sub&gt;p&lt;/sub&gt; cal/mol/K</th>
</tr>
</thead>
<tbody>
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### Results of Group Additivity Optimisation

As with the molar entropy values for many species there are also only a limited number of studies that report heat capacity values. A comparison of literature and group additivity specific heat capacities at constant pressure is included in Table XCI1.
Table XCVI shows the THERM groups that express the largest differences between the new and old groups, many of the old groups originate from Benson. The majority of the group values applicable to stable alkane and alkene species have only changed by marginal amounts. The value for the heat of formation for the ‘VINS’ group has been increased by 2.04 kcal mol⁻¹ which results in relatively good agreement between the GA predictions for thermochemical data and the literature values for the C₃H₅-t and C₄H₇-2-2 radicals. Further study of the thermodynamic properties of the C₃H₅ and C₄H₇ radicals is recommended in order accurately quantify the associated uncertainty.

The biggest changes were made to the groups used to calculate thermochemical data for oxygenated species and for some radical groups. The group values for the heat of formation of n-alcohols have changed by small amounts. However, the values for the standard molar entropy has changed by approximately 1 cal K⁻¹ mol⁻¹. The previous group values (O/C/H and ALKoxy) resulted in standard molar entropies for n-alcohols that were significantly lower than those found in the literature. The group value for the heat of formation for the alkoy group has increased by 0.86 cal K⁻¹ mol⁻¹. Further study of the thermodynamic properties of the C₃H₅-O radicals is recommended in order accurately quantify the associated uncertainty.

New groups were added to describe thermochemical data for alcohol hydroperoxides (C/C/H/O/OO and C/C₂/O/OO) as these groups were not present prior to this study. Table XCII compares the thermodynamic properties calculated theoretically¹²⁷,¹²⁸ and using the new group values.

Using the previous values for alkyl hydroperoxide species (ALPEROX, C/C/H/O/OO and C/C₂/O/OO) resulted in heats of formation that were approximately 2 kcal mol⁻¹ lower than the literature values. Standard molar entropy values were approximately 1.70 cal K⁻¹ mol⁻¹ higher than the literature values.

### TABLE XCVII: Specific heat capacities at constant pressure.

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### TABLE XCVI: Radicals as implemented by THERM.
C\textsubscript{1}–C\textsubscript{4} thermochemical properties: updated group additivity groups

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<td>0.22</td>
<td>−2.05</td>
<td>−2.84</td>
<td>−3.55</td>
<td>−4.09</td>
<td>−4.72</td>
<td>−4.97</td>
</tr>
<tr>
<td>New</td>
<td>85.27</td>
<td>−0.48</td>
<td>−1.17</td>
<td>−1.78</td>
<td>−3.74</td>
<td>−3.25</td>
<td>−3.68</td>
<td>−3.74</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>1.03</td>
<td>0.70</td>
<td>−0.88</td>
<td>−1.06</td>
<td>−0.81</td>
<td>−0.84</td>
<td>−1.04</td>
<td>−1.23</td>
</tr>
</tbody>
</table>

**TABLE XCVI:** Groups that have undergone the largest changes
VI. CONCLUSIONS

A thorough literature review of thermochemical properties was undertaken for C$_1$–C$_4$ alkanes, alkenes, alcohols, hydroperoxides and alcoholic hydroperoxides and their associated radicals from a variety of sources: high level *ab initio* studies, experimental studies, online databases, and review studies. The current work not only collated values for the heats of formation of small stable species but includes a review of literature molar entropies and heat capacities of both stable and radical species.

This study highlights the importance of carrying out a thorough search of available data in-order to identify the most accurate thermochemical properties for a species, as within the literature there can be significant differences between values of perceived high quality. In general values for the enthalpy of formation for stable species shows relatively good agreement and therefore are well known. There are less values available in the literature for molar entropies and as such the uncertainties are more difficult to quantify, likewise for many radical species for both molar entropy and enthalpy of formation.

The literature values were compared to the values obtained using a group additivity method as devised by Benson$^6$. The group values were optimised to best represent the most accurate thermochemical data available by iterative and hierarchical means. New groups have been added in order to estimate thermochemical properties of alcoholic hydroperoxide species. The adoption of the new groups has increased the predictive ability of the group additivity method employed and thermochemical data can now be estimated for larger combustion relevant species for which no calculations or measurements exist with increased confidence.

The approach employed in this study has resulted in improved agreement between group additivity and literature data for species such as the alcohol hydroperoxides without affecting the agreement the performance of the group values for species that are well known such as alkanes. The consistent approach means that this method can be used to increase the predictive power of group additivity for other classes of hydrocarbons such as esters, ethers, alkynes and aromatics.

39. J. M. Nicovich, C. A. Van Dijk, K. D. Kreutter, and P. H. Wine,
C$_1$–C$_4$ thermochemical properties: updated group additivity groups
thermochemical properties: updated group additivity groups


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