



Critical evaluation of thermochemical properties of C-1-C-4 species: updated group-contributions to estimate thermochemical properties

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Critical evaluation of thermochemical properties of C₁–C₄ species; updated group-contributions to estimate thermochemical properties.

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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 K) and entropy, ΔS° 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 Thermochemical Tables (ATcT),² Third Millennium Thermodynamic Database³ and from numerous experimental and theoretical studies. A recent *ab 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 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 Benson⁶ 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 THERM⁷ computer programme employs the group additivity (GA) method developed by Benson⁶ and can be used to estimate, edit, or enter thermody-

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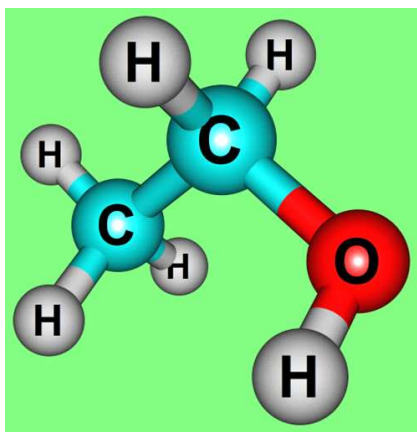


FIG. 1. How group additivity (GA) is utilised in THERM for a sample species. Symmetry: $\sigma_{int} = 3$, Rotors: 2.

dynamic property data for gas phase molecules and radicals. THERM can generate thermochemistry of a stable molecule in NASA polynomial format⁸ 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 1976.⁶ 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^{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, $\bar{x} = \sum_i^n(x_i)/n$. 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-in⁹) by varying the property value from the existing group additivity values, Γ_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 2σ uncertainty was chosen to quantify the expected accuracy of each property as discussed by Ruscic¹⁰; 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 C₁–C₄ 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 \S°). Note that the term **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

CBS-QB3, CBS-4, CBS-Q, CBS-Q/APNO, G1-4, W1: quantum chemistry composite methods

QCISDT: RQCISD(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

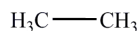
SLIF: Saturated Laser-Induced Fluorescence

MP 2-4: 2nd to 4th order MöllerPlesset perturbation theory

PM3: Parameterized Model number 3

A. Alkanes and alkyl radicals

1. Ethane



The thermodynamic properties of ethane have been studied extensively^{4,11,13-22} as shown in Tables I and II.

The average heat of formation for ethane is -20.16 kcal mol⁻¹ with a standard deviation of 0.30 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 kcal mol⁻¹. Optimisation of the groups results in an heat of formation of -20.02 kcal mol⁻¹.

The average molar entropy for ethane is 54.76 cal K⁻¹ mol⁻¹ with a standard deviation of 0.06 cal K⁻¹ mol⁻¹. Cao and Back¹⁵'s recommendation is 0.14 cal K⁻¹ 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.

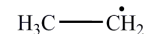
Literature	$\Delta_f H^\circ$	Year	Source
Prosen and Rossini ¹³	-20.24	1945	Rev.
Pitmann and Pilcher ¹⁴	-20.24	1972	Exp.*
Chao <i>et al.</i> ¹¹	-20.24	1973	Calc.**
Cao and Back ¹⁵	-20.20	1984	Exp.†
Lange's Handbook ²¹	-20.19	1999	Rev.
Manion ¹⁶	-20.00 ± 0.10	1986	Rev.
Kollais <i>et al.</i> ¹⁸	-20.10	2005	Calc.‡
Baulch <i>et al.</i> ¹⁷	-20.00	2005	Rev.
Rayne and Forest ¹⁹	-19.81	2010	Calc.§
Rayne and Forest ¹⁹	-21.18	2010	Calc.§
CRC ²²	-20.08	1999	Rev.
3 rd Millennium ³	-20.04	2012	
Goldsmith <i>et al.</i> ⁴	-20.00 ± 0.10	2012	Calc.¶
Verevkin <i>et al.</i> ⁵	-20.08	2013	Rev.
<i>Standard Deviation</i>	<i>0.30</i>		
Recommendation	-20.08		
GA	-20.02		
* CALORIMETRY	** RRHO		
† KINETICS	‡ DMC		
§ G4	§ W1BD		
¶ QCISDT			

TABLE I. Enthalpy of formation (kcal mol⁻¹) of ethane.

Literature	S°	Year	Source
Chao <i>et al.</i> ¹¹	54.76	1973	Calc.*
Cao and Back ¹⁵	54.90	1984	Exp.**
Lange's Handbook ²¹	54.76	1999	Rev.
Baulch <i>et al.</i> ¹⁷	54.70	2005	Rev.
De Tar ²⁰	54.73	2007	Rev.
CRC ²²	54.78	1999	Rev.
3 rd Millennium ³	54.78	2012	
Goldsmith <i>et al.</i> ⁴	54.70 ± 0.6	2012	Calc.†
<i>Standard Deviation</i>	<i>0.06</i>		
Recommendation	54.74		
GA	54.84		
* RRHO	** KINETICS		
† QCISDT			

TABLE II. Molar entropy (cal K⁻¹ mol⁻¹) of ethane.

2. Ethyl radical



Tables III and IV contain literature values for the heat of formation and molar entropy of the ethyl radical. As with most of the species included in this study there are more values available for the heat of formation (Table III) compared to the molar entropy (Table IV).

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

Literature	$\Delta_f H^\circ$	Year	Source
Cao and Back ¹⁵	28.00	1984	Exp.*
Brouard <i>et al.</i> ²³	28.36 \pm 0.40	1986	Exp.*
Seakins <i>et al.</i> ²⁴	28.92 \pm 0.36	1992	Exp.*
NIST (Tsang ²⁵)	28.40	1996	Rev.
Kollais <i>et al.</i> ¹⁸	26.40	2005	Calc.**
Baulch <i>et al.</i> ¹⁷	28.90	2005	Rev.
Bodi <i>et al.</i> ²⁶	28.84	2006	Exp.†
3 rd Millennium ³	28.61	2012	
Goldsmith <i>et al.</i> ⁴	28.90 \pm 0.40	2012	Calc.‡
<i>Standard Deviation</i>	0.75		
Recommendation	28.65		
GA	28.65		

* KINETICS ** DMC
† TPEPICO ‡ QCISDT

TABLE III. Enthalpy of formation (kcal mol⁻¹) of ethyl radical.

Literature	S°	Year	Source
Cao and Back ¹⁵	59.00	1984	Exp.*
Seakins <i>et al.</i> ²⁴	61.18 \pm 1.67	1992	Exp.*
3 rd Millennium ³	58.07	2012	
Goldsmith <i>et al.</i> ⁴	59.10 \pm 0.50	2012	Calc.**
<i>Standard Deviation</i>	1.02		
Recommendation	59.29		
GA	59.29		

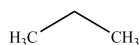
* KINETICS ** QCISDT

TABLE IV. Molar entropy (cal K⁻¹ mol⁻¹) of ethyl radical.

authors stated that the results using this method are less accurate those that using higher-levels of theory. When the Kollais *et al.*¹⁸ value is excluded the average becomes 28.65 kcal mol⁻¹. Optimisation of the groups results in an heat of formation of 28.65 kcal mol⁻¹.

The average of the literature values for the molar entropy is 59.29 cal K⁻¹ mol⁻¹ with a standard deviation of 1.02 K⁻¹ mol⁻¹. All values are within two standard deviations of the average.

3. Propane



Thermodynamic properties for propane has been the subject of several studies.^{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⁻¹ with a standard deviation of 0.12 kcal mol⁻¹. The value from Goldsmith *et al.*⁴ differs from the average by 0.25 kcal mol⁻¹ which is more than twice the standard deviation. When it is excluded the average becomes -24.92 kcal mol⁻¹. Optimisation of the groups results in an heat of formation of -25.02

Literature	$\Delta_f H^\circ$	Year	Source
Prosen and Rossini ¹³	-24.82 \pm 0.14	1945	Rev.
Pitmann and Pilcher ¹⁴	-25.02	1972	Exp.*
Chao <i>et al.</i> ¹¹	-24.82	1973	Calc.**
Cao and Back ¹⁵	-20.20	1984	Exp.†
Lange's Handbook ²¹	-20.19	1999	Rev.
Manion ¹⁶	-20.00 \pm 0.10	1986	Rev.
Kollais <i>et al.</i> ¹⁸	-20.10	2005	Calc.‡
Baulch <i>et al.</i> ¹⁷	-25.00	2005	Rev.
CRC ²²	-24.80	2011	Rev.
3 rd Millennium ³	-25.02	2012	
Goldsmith <i>et al.</i> ⁴	-25.50 \pm 0.30	2012	Calc.§
ATcT ²	-24.95 \pm 0.04	2012	Calc.¶
Verevkin <i>et al.</i> ⁵	-24.98	2013	Rev.
<i>Standard Deviation</i>	0.12		
Recommendation	-24.92		
GA	-25.02		

* CALORIMETRY ** RRHO
† KINETICS ‡ DMC
§ QCISDT ¶ TN

TABLE V. Enthalpy of formation (kcal mol⁻¹) of propane.

Literature	S°	Year	Source
Chao <i>et al.</i> ¹¹	64.58	1973	Calc.*
Lange's Handbook ²¹	64.58	1999	Rev.
Baulch <i>et al.</i> ¹⁷	64.60	2005	Rev.
De Tar ²⁰	64.77	2007	Rev.
CRC ²²	64.58	2011	Rev.
3 rd Millennium ³	64.10	2012	
Goldsmith <i>et al.</i> ⁴	66.10 \pm 1.20	2012	Calc.**
<i>Standard Deviation</i>	0.50		
Recommendation	64.63		
GA	64.49		

* RRHO ** QCISDT

TABLE VI. Molar entropy (cal K⁻¹ mol⁻¹) of propane.

kcal mol⁻¹.

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

4. n-Propyl radical

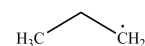


Table VII contains heat of formation values and Table VIII molar entropy values for the *n*-propyl radical. In general there is good agreement amongst both the $\Delta_f H^\circ$ (298.15 K) and S° (298.15 K) data that spans over

Literature	$\Delta_f H^\ominus$	Year	Source
Castelhano and Griller ²⁸	22.80	1982	Exp.*
Holmes <i>et al.</i> ²⁹	22.70	1988	Exp.**
Tsang ²⁵	23.95	1996	Rev.
Seetula and Slagle ³⁰	24.09 ±0.50	1997	Exp.*
Baulch <i>et al.</i> ¹⁷	24.00	2005	Rev.
Bodi <i>et al.</i> ²⁶	24.21 ±0.24	2006	Exp.†
3 rd Millennium ³	24.21	2012	
Goldsmith <i>et al.</i> ⁴	24.30 ±0.90	2012	Calc.‡
<i>Standard Deviation</i>	0.61		
Recommendation	23.78		
GA	24.03		

* KINETICS ** MEI
† TPEPICO ‡ QCISDT

TABLE VII. Enthalpy of formation (kcal mol⁻¹) of *n*-propyl radical.

Literature	S^\ominus	Year	Source
Tsang ²⁵	69.17	1996	Rev.
Seetula and Slagle ³⁰	67.88 ±1.20	1997	Exp.*
Baulch <i>et al.</i> ¹⁷	69.20	2005	Rev.
3 rd Millennium ³	69.34	2012	Calc.**
Goldsmith <i>et al.</i> ⁴	69.30 ±1.0	2012	Calc.**
<i>Standard Deviation</i>	0.72		
Recommendation	69.25		
GA	69.18		

* KINETICS ** QCISDT

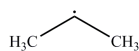
TABLE VIII. Molar entropy (cal K⁻¹ mol⁻¹) of *n*-propyl radical.

thirty years.

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. 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 *iso*-propyl radical is 20.89 cal 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 *et al.*²⁹ which is 1.80 cal K⁻¹ mol⁻¹ smaller than the average. When this value is excluded

Literature	$\Delta_f H^\ominus$	Year	Source
Castelhano and Griller ²⁸	19.19	1982	Exp.*
Holmes <i>et al.</i> ²⁹	19.09	1988	Exp.**
Seetula and Slagle ³¹	20.75 ±0.50	1990	Exp.*
Tsang ³²	22.29 ±0.60	1996	Rev.
Seetula and Slagle ³⁰	20.69±0.50	1997	Exp.*
Tschuikow-Roux and Chen ³³	21.00 ±0.50	1992	Exp.*
Seakins <i>et al.</i> ²⁴	21.51 ±0.41	1992	Exp.*
Baulch <i>et al.</i> ¹⁷	21.50	2005	Rev.
Bodi <i>et al.</i> ²⁶	21.15 ±0.24	2006	Exp.§
3 rd Millennium ³	21.55	2012	
Goldsmith <i>et al.</i> ⁴	21.20 ±0.90	2012	Calc.†
<i>Standard Deviation</i>	0.97		
Recommendation	20.77		
GA	20.95		

* KINETICS ** MEI
§ TPEPICO † QCISDT

TABLE IX. Enthalpy of formation (kcal mol⁻¹) of *iso*-propyl radical.

Literature	S^\ominus	Year	Source
Tsang ²⁵	69.23	1996	Rev.
Seetula and Slagle ³⁰	67.16 ±1.20	1997	Exp.*
Baulch <i>et al.</i> ¹⁷	69.10	2005	Rev.
3 rd Millennium ³	69.42	2012	
Goldsmith <i>et al.</i> ⁴	68.90 ±0.80	2012	Calc.**
<i>Standard Deviation</i>	0.81		
Recommendation	69.24		
GA	68.75		

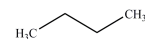
* KINETICS ** QCISDT

TABLE X. Molar entropy (cal K⁻¹ mol⁻¹) of *iso*-propyl radical.

average becomes 20.77 cal K⁻¹ mol⁻¹. Optimisation of the groups results in a heat of formation of 20.95 cal 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 Slagle³⁰ 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. n-Butane



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

The average heat of formation for *n*-butane is -29.99 kcal mol⁻¹ with a standard deviation of 0.17 kcal

Literature	$\Delta_f H^\circ$	Year	Source
Prosen and Rossini ¹³	-30.37 ± 0.18	1945	Rev.
Pitmann and Pilcher ¹⁴	-30.03 ± 0.15	1972	Exp.*
Lange's Handbook ²¹	-30.02	1999	Rev.
Baulch <i>et al.</i> ¹⁷	-30.10	2005	Rev.
Rayne and Forest ¹⁹	-29.54	2010	Calc.**
CRC ²²	-30.04	2011	Rev.
3 rd Millennium ³	-30.06	2012	
Goldsmith <i>et al.</i> ⁴	-30.00 ± 0.10	2012	Calc.†
ATcT ²	-30.09 ± 0.09	2012	Calc.‡
Verevkin <i>et al.</i> ⁵	-30.16	2013	Rev.
<i>Standard Deviation</i>	<i>0.17</i>		
Recommendation	-30.04		
GA	-30.02		

* CALORIMETRY

** G4

† QCISDT

‡ TN

TABLE XI. Enthalpy of formation (kcal mol⁻¹) of *n*-butane.

Literature	S°	Year	Source
Chen <i>et al.</i> ³⁴	74.07	1975	Calc.*
Lange's Handbook ²¹	74.11	1999	Rev.
Baulch <i>et al.</i> ¹⁷	74.00	2005	Rev.
De Tar ²⁰	74.35	2007	Rev.
3 rd Millennium ³	74.06	2012	
Goldsmith <i>et al.</i> ⁴	73.70 ± 2.00	2012	Calc.**
<i>Standard Deviation</i>	<i>0.17</i>		
Recommendation	74.05		
GA	74.14		

* RRHO

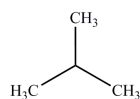
** QCISDT

TABLE XII. Molar entropy (cal K⁻¹ mol⁻¹) of *n*-butane.

mol⁻¹. The Rayne and Forest¹⁹ recommendation differs from the average by 0.45 kcal mol⁻¹ which is more than two standard deviations. 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 C₄H₁₀ 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 Rossini¹³ differs from the average by 0.64 kcal mol⁻¹

Literature	$\Delta_f H^\circ$	Year	Source
Prosen and Rossini ¹³	-31.45 ± 0.16	1945	Rev.
Pitmann and Pilcher ¹⁴	-32.07 ± 0.14	1972	Exp.*
Chen <i>et al.</i> ³⁴	-32.18	1975	Exp.**
Lange's Handbook ²¹	-32.07	1999	Rev.
Baulch <i>et al.</i> ¹⁷	-32.20	2005	Rev.
CRC ²²	-32.07	2011	Rev.
3 rd Millennium ³	-32.26	2012	
Goldsmith <i>et al.</i> ⁴	-32.00 ± 0.40	2012	†
ATcT ²	-32.35 ± 0.10	2012	Calc.‡
Verevkin <i>et al.</i> ⁵	-32.24	2013	Rev.
<i>Standard Deviation</i>	<i>0.24</i>		
Recommendation	-32.16		
GA	-32.17		

* CALORIMETRY

** RRHO

† QCISDT

‡ TN

TABLE XIII. Enthalpy of formation (kcal mol⁻¹) of *iso*-butane.

Literature	S°	Year	Source
Chen <i>et al.</i> ³⁴	70.60	1973	Calc.*
Lange's Handbook ²¹	70.41	1999	Rev.
Baulch <i>et al.</i> ¹⁷	70.60	2005	Rev.
De Tar ²⁰	74.35	2007	Rev.
3 rd Millennium ³	70.62	2012	
Goldsmith <i>et al.</i> ⁴	71.20 ± 1.90	2012	Calc.**
<i>Standard Deviation</i>	<i>0.27</i>		
Recommendation	70.70		
GA	70.71		

* RRHO

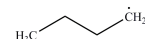
** QCISDT

TABLE XIV. Molar entropy (cal K⁻¹ mol⁻¹) of *iso*-butane.

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



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 Database³ 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

Literature	$\Delta_f H^\ominus$	Year	Source
Holmes <i>et al.</i> ²⁹	18.09	1988	Exp.*
Seetula and Slagle ³¹	19.33 ± 0.50	1990	Exp.**
Tsang ³²	22.29 ± 0.60	1996	Rev.
Seetula and Slagle ³⁰	20.69 ± 0.53	1997	Exp.*
Knyazev and Slagle ³⁵	20.10 ± 0.53	1997	Exp.*
Seakins <i>et al.</i> ²⁴	21.51 ± 0.41	1992	Exp.*
Baulch <i>et al.</i> ¹⁷	19.20	2005	Rev.
3 rd Millennium ³	19.55	2012	
Goldsmith <i>et al.</i> ⁴	19.30 ± 0.90	2012	Calc.†
<i>Standard Deviation</i>	0.60		
Recommendation	19.26		
GA	19.03		

* MEI ** KINETICS
† QCISDT

TABLE XV. Enthalpy of formation (kcal mol⁻¹) of *n*-butyl radical.

Literature	S^\ominus	Year	Source
Seetula and Slagle ³⁰	78.63 ± 1.20	1997	Exp.*
Baulch <i>et al.</i> ¹⁷	79.30	2005	Rev.
3 rd Millennium ³	73.52	2012	
Goldsmith <i>et al.</i> ⁴	78.50 ± 1.70	2012	Calc.**
<i>Standard Deviation</i>	1.98		
Recommendation	78.74		
GA	78.83		

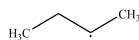
* KINETICS ** QCISDT

TABLE XVI. Molar entropy (cal K⁻¹ mol⁻¹) of *n*-butyl radical.

with the average within twice the standard deviation. Optimisation of the groups results in a heat of formation of 19.03 kcal mol⁻¹.

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 3rdMillennium database³ 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 Database³ 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 Castelhana and Griller²⁸ differs

Literature	$\Delta_f H^\ominus$	Year	Source
Castelhana and Griller ²⁸	13.91	1982	Exp.*
Holmes <i>et al.</i> ²⁹	15.29	1988	Exp.**
Seetula and Slagle ³¹	15.94 ± 0.50	1990	Exp.*
Tsang ³²	16.99 ± 0.40	1985	Rev.
Tsang ²⁵	16.49 ± 0.50	1996	Rev.
Seetula and Slagle ³⁰	15.94 ± 0.50	1997	Exp.*
Seakins <i>et al.</i> ²⁴	16.13 ± 0.53	1992	Exp.*
3 rd Millennium ³	16.78	2012	Calc.†
Goldsmith <i>et al.</i> ⁴	16.60 ± 0.90	2012	Calc.†
<i>Standard Deviation</i>	0.84		
Recommendation	16.11		
GA	15.95		

* KINETICS ** MEI
† QCISDT

TABLE XVII. Enthalpy of formation (kcal mol⁻¹) of *s*-butyl radical.

Literature	S^\ominus	Year	Source
Seakins <i>et al.</i> ²⁴	81.98 ± 2.15	1992	Exp.*
Seetula and Slagle ³⁰	78.78 ± 1.20	1997	Exp.*
3 rd Millennium ³	76.88	2012	Calc.**
Goldsmith <i>et al.</i> ⁴	79.00 ± 1.50	2012	
<i>Standard Deviation</i>	1.52		
Recommendation	79.34		
GA	79.77		

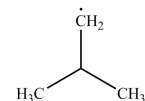
* 2nd CALCULATION ** QCISDT

TABLE XVIII. Molar entropy (cal K⁻¹ mol⁻¹) of *s*-butyl radical.

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

Literature	$\Delta_f H^\circ$	Year	Source
Holmes <i>et al.</i> ²⁹	15.80	1988	Exp.*
Seetula and Slagle ³¹	17.37±0.50	1990	Exp.**
Tsang ²⁵	17.00 ±0.50	1996	Rev.
Baulch <i>et al.</i> ¹⁷	17.40	2005	Rev.
3 rd Millennium ³	17.63	2012	
Goldsmith <i>et al.</i> ⁴	17.80 ±0.90	2012	Calc.†
<i>Standard Deviation</i> 0.63			
Recommendation 17.32			
GA 17.33			
* MEI		** KINETICS	
† QCISDT			

TABLE XIX. Enthalpy of formation (kcal mol⁻¹) of *iso*-butyl radical.

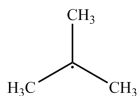
Literature	S°	Year	Source
Seetula and Slagle ³⁰	75.52±1.20	1997	Exp.*
Baulch <i>et al.</i> ¹⁷	76.40	2005	Rev.
3 rd Millennium ³	72.82	2012	Calc.**
Goldsmith <i>et al.</i> ⁴	76.40 ±1.60	2012	Calc.*
<i>Standard Deviation</i> 1.32			
Recommendation 75.33			
GA 75.34			
* 2 nd CALCULATION		** QCISDT	

TABLE XX. Molar entropy (cal K⁻¹ mol⁻¹) of *iso*-butyl radical.

is more than twice the standard deviation. When it is excluded the average becomes 17.33 kcal mol⁻¹.

The average molar entropy of the *iso*-butyl radical is 75.33 cal K⁻¹ mol⁻¹ with a standard deviation of 1.32 cal K⁻¹ mol⁻¹. All of the values in Table XX 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

Literature	$\Delta_f H^\circ$	Year	Source
McMillen and Golden ³⁶	8.70	1982	Rev.
Castelhano and Griller ²⁸	9.39	1982	Exp.*
Holmes <i>et al.</i> ²⁹	9.49	1988	Exp.**
Russell <i>et al.</i> ³⁷	11.61 ±0.80	1988	Exp.*
Richards <i>et al.</i> ³⁸	11.49 ±0.40	1990	Exp.*
Seetula and Slagle ³¹	12.38 ±0.50	1990	Exp.*
Nicovich <i>et al.</i> ³⁹	12.09 ±0.80	1991	Exp.*
Seakins and Pilling ⁴⁰	12.26 ±0.43	1991	Exp.*
Berkowitz <i>et al.</i> ⁴¹	12.61	1994	Rev.
Tsang ²⁵	11.00 ±0.50	1996	Rev.
Smith and Radom ⁴²	13.62 ±1.67	1996	Calc.†
Marsi <i>et al.</i> ⁴³	10.70 ±0.30 – 0.60	2000	Calc.‡
Srinivasan <i>et al.</i> ⁴⁴	12.80 ±2.00	2000	Calc.§
Baulch <i>et al.</i> ¹⁷	12.30	2005	Rev.
3 rd Millennium ³	13.15	2012	
Goldsmith <i>et al.</i> ⁴	13.00 ±0.90	2012	Calc.∥
<i>Standard Deviation</i> 1.27			
Recommendation 11.86			
GA 11.87			
* KINETICS		** MEI	
† G2		‡ CBS-4	
§ RRKM		∥ QCISDT	

TABLE XXI. Enthalpy of formation (kcal mol⁻¹) of *tert*-butyl radical.

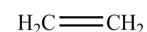
Literature	S°	Year	Source
Russell <i>et al.</i> ³⁷	75.53±1.67	1988	Exp.*
Seetula and Slagle ³¹	75.29 ±0.96	1990	Exp.*
Seakins and Pilling ⁴⁰	74.84 ±1.20	1991	Exp.*
Baulch <i>et al.</i> ¹⁷	75.80	2005	Rev.
3 rd Millennium ³	77.05	2012	Calc.†
Goldsmith <i>et al.</i> ⁴	76.20±1.4	2012	Calc.‡
<i>Standard Deviation</i> 0.79			
Recommendation 75.84			
GA 75.85			
* KINETICS		** MEI	
** CBS		‡ QCISDT	

TABLE XXII. Molar entropy (cal K⁻¹ mol⁻¹) of *tert*-butyl radical.

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

Literature	$\Delta_f H^\circ$	Year	Source
Chao and Zwolinski ¹²	12.55	1975	Calc.*
Chase ⁴⁵	12.54	1998	Rev.
Lange's Handbook ²¹	12.50	1999	Rev.
Baulch <i>et al.</i> ¹⁷	12.50	2005	Rev.
Rayne and Forest ¹⁹	12.57	2010	Calc.**
Rayne and Forest ¹⁹	11.95	2010	Calc.†
CRC ²²	12.52	2011	Rev.
3 rd Millennium ³	12.5	2012	
Goldsmith <i>et al.</i> ⁴	12.50 ±0.10	2012	Calc.‡
ATcT ²	12.56 ±0.04	2012	Calc.§
Verevkin <i>et al.</i> ⁵	12.55	2013	Rev.
<i>Standard Deviation</i>	0.03		
Recommendation	12.53		
GA	12.56		

* RRHO ** W1BD
† G4 ‡ QCISDT
§ TN

TABLE XXIII. Enthalpy of formation (kcal mol⁻¹) of ethylene.

Literature	S°	Year	Source
Chase ⁴⁵	52.42	1998	Rev.
Lange's Handbook ²¹	52.34	1999	Rev.
Baulch <i>et al.</i> ¹⁷	52.40	2005	Rev.
CRC ²²	52.41	2011	Rev.
3 rd Millennium ³	52.42	2012	
Goldsmith <i>et al.</i> ⁴	52.30 ±0.40	2012	Calc.*
<i>Standard Deviation</i>	0.05		
Recommendation	52.38		
GA	52.43		

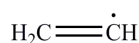
* QCISDT

TABLE XXIV. Molar entropy (cal K⁻¹ mol⁻¹) of ethylene.

kcal mol⁻¹ with a standard deviation of 0.03 kcal mol⁻¹. All of the values in Table XXIII agree with the average within twice the standard deviation. Optimisation of the groups results in a heat of formation of 12.56 kcal mol⁻¹.

The average molar entropy for ethylene is 52.38 cal K⁻¹ mol⁻¹ with a standard deviation of 0.05 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



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

Literature	$\Delta_f H^\circ$	Year	Source
Lias <i>et al.</i> ⁴⁶	63.33	1988	Rev.
Parmar and Benson ⁴⁷	66.90 ±0.41	1988	Exp.*
Russell <i>et al.</i> ⁴⁸	67.10 ±0.60	1989	Exp.*
Berkowitz <i>et al.</i> ⁴¹	71.60 ±0.79	1994	Rev.
Kaiser and Wallington ⁴⁹	70.60 ±0.40	1996	Exp.*
Knyazev and Slagle ⁵⁰	71.39 ±1.60	1996	Calc.*
Tsang ²⁵	71.60±1.20	1996	Rev.
Glukhovtsev and Bach ⁵¹	72.04	1998	Calc.**
Lange's Handbook ²¹	69.10	1999	Rev.
Baulch <i>et al.</i> ¹⁷	71.60	2005	Rev.
Tabor <i>et al.</i> ⁵²	71.06 ±0.31	2012	Calc.†
3 rd Millennium ³	70.88	2012	Calc.†
Goldsmith <i>et al.</i> ⁴	71.20 ±0.20	2012	Calc.‡
<i>Standard Deviation</i>	2.57		
Recommendation	70.36		
GA	70.99		

* KINETICS ** G2
† HEAT ‡ QCISDT

TABLE XXV. Enthalpy of formation (kcal mol⁻¹) of ethenyl radical.

Literature	S°	Year	Source
Russell <i>et al.</i> ⁴⁸	55.90 ±2.60	1989	Exp.*
Lange's Handbook ²¹	56.40	1999	Rev.
Baulch <i>et al.</i> ¹⁷	55.90	2005	Rev.
3 rd Millennium ³	55.85	2012	
Goldsmith <i>et al.</i> ⁴	55.85 ±0.20	2012	Calc.**
<i>Standard Deviation</i>	0.22		
Recommendation	55.96		
GA	56.34		

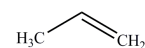
* KINETICS ** QCISDT

TABLE XXVI. Molar entropy (cal K⁻¹ mol⁻¹) of ethenyl radical.

radical is 69.78 kcal mol⁻¹ with a standard deviation of 2.57 kcal mol⁻¹. The value from Lias *et al.*⁴⁶ 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 70.99 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



Values for the heat of formation of propene vary from 3.72¹⁹ to 5.60¹⁸ 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

Literature	$\Delta_f H^\ominus$	Year	Source
Furuyama <i>et al.</i> ⁵³	4.88	1975	Exp.*
Lange's Handbook ²¹	4.78	1999	Rev.
Kollais <i>et al.</i> ¹⁸	5.60	2005	Calc.**
Baulch <i>et al.</i> ¹⁷	4.80	2005	Rev.
Rayne and Forest ¹⁹	5.04	2010	Calc.†
Rayne and Forest ¹⁹	3.72	2010	Calc.‡
CRC ²²	4.78	2011	Rev.
3 rd Millennium ³	4.78	2012	
Goldsmith <i>et al.</i> ⁴	4.60 ± 0.30	2012	Calc.§
ATcT ²	4.86 ± 0.08	2012	Calc.
Verevkin ⁵	4.45	2013	Rev.
<i>Standard Deviation</i>	<i>0.43</i>		
Recommendation	4.68		
GA	<i>4.92</i>		
* KINETICS	** DMC		
† G4	‡ W1BD		
§ QCISDT	TN		

TABLE XXVII. Enthalpy of formation (kcal mol⁻¹) of propene.

Literature	S^\ominus	Year	Source
Lange's Handbook ²¹	63.72	1999	Rev.
Baulch <i>et al.</i> ¹⁷	63.70	2005	Rev.
3 rd Millennium ³	63.73	2012	
Goldsmith <i>et al.</i> ⁴	63.60 ± 0.90	2012	Calc.*
<i>Standard Deviation</i>	<i>0.09</i>		
Recommendation	63.64		
GA	<i>63.53</i>		
* QCISDT			

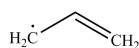
TABLE XXVIII. Molar entropy (cal K⁻¹ mol⁻¹) of propene.

in Table XXVIII.

The average heat of formation for propene is 4.76 kcal mol⁻¹ with a standard deviation of 0.43 kcal mol⁻¹. The value from Kollais *et al.*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

Literature	$\Delta_f H^\ominus$	Year	Source
Rossi and Golden ⁵⁴	39.40 ± 1.50	1979	Exp.*
Traeger ⁵⁵	39.48 ± 0.79	1984	Exp.**
Tsang ²⁵	40.90	1996	Rev.
Baulch <i>et al.</i> ¹⁷	40.80	2005	Rev.
Lee and Bozzelli ⁵⁶	40.06	2005	Calc.†
Tabor <i>et al.</i> ⁵²	40.29 ± 0.43	2012	Calc.‡
3 rd Millennium ³	39.10	2012	
Cord <i>et al.</i> ⁵⁷	39.50	2012	Calc.§
Goldsmith <i>et al.</i> ⁴	40.60 ± 0.90	2012	Calc.
<i>Standard Deviation</i>	<i>0.63</i>		
Recommendation	40.16		
GA	<i>40.72</i>		
* KINETICS	** PMS		
† B3LYP	‡ HEAT		
§ CBS-QB3	QCISDT		

TABLE XXIX. Enthalpy of formation (kcal mol⁻¹) of allyl radical.

Literature	S^\ominus	Year	Source
Lange's Handbook ²¹	62.14	1999	Rev.
Baulch <i>et al.</i> ¹⁷	62.00	2005	Rev.
Lee and Bozzelli ⁵⁶	62.94	2005	Calc.*
3 rd Millennium ³	61.87	2012	
Cord <i>et al.</i> ⁵⁷	63.00	2012	Calc.**
Goldsmith <i>et al.</i> ⁴	61.50 ± 0.80	2012	Calc.†
<i>Standard Deviation</i>	<i>0.55</i>		
Recommendation	62.24		
GA	<i>62.56</i>		
* B3LYP	** CBS-QB3		
† QCISDT			

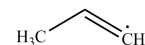
TABLE XXX. Molar entropy (cal K⁻¹ mol⁻¹) of allyl radical.

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 62.56 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^{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 param-

Literature	$\Delta_f H^\ominus$	Year	Source
Wu and Kern ⁵⁹	62.80	187	Exp.*
Baulch <i>et al.</i> ¹⁷	62.80	2005	Rev.
3 rd Millennium ³	63.46	2012	
Goldsmith <i>et al.</i> ⁴	64.10 ± 0.90	2012	Calc.**
<i>Standard Deviation</i> 0.54			
Recommendation 63.29			
GA	63.35		
* KINETICS	** QCISDT		

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

Literature	S^\ominus	Year	Source
Baulch <i>et al.</i> ¹⁷	64.80	2005	Rev.
3 rd Millennium ³	64.84	2012	
Goldsmith <i>et al.</i> ⁴	94.90 ± 0.90	2012	Calc.*
<i>Standard Deviation</i> 0.04			
Recommendation 64.86			
GA	64.69		
* QCISDT			

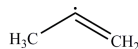
TABLE XXXII. Molar entropy (cal K⁻¹ mol⁻¹) of 1-propenyl radical.

ters.

The average of the heat of formation values is 63.29 kcal mol⁻¹ with a standard deviation of 0.54 kcal mol⁻¹. All of the values in Table XXXI agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is 63.35 kcal mol⁻¹.

The average molar entropy is 64.86 cal K⁻¹ mol⁻¹ with a standard deviation of 0.04 cal K⁻¹ mol⁻¹. All of the values in Table XXXII agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is 64.69 cal K⁻¹ mol⁻¹.

6. 2-Propenyl radical



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 val-

Literature	$\Delta_f H^\ominus$	Year	Source
Wu and Kern ⁵⁹	56.80	1987	Exp.*
3 rd Millennium ³	56.80	2012	Calc.†
Goldsmith <i>et al.</i> ⁴	58.03 ± 0.90	2012	Calc.**
<i>Standard Deviation</i> 1.74			
Recommendation 58.03			
GA	59.78		
* KINETICS	** QCISDT		

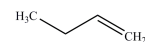
TABLE XXXIII. Enthalpy of formation (kcal mol⁻¹) of 2-propenyl radical.

Literature	S^\ominus	Year	Source
3 rd Millennium ³	63.59	2012	
Goldsmith <i>et al.</i> ⁴	65.40 ± 0.80	2012	Calc.*
<i>Standard Deviation</i> 0.91			
Recommendation 64.50			
GA	64.84		
* QCISDT			

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

ues 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.

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

Literature	$\Delta_f H^\ominus$	Year	Source
Prosen <i>et al.</i> ⁶⁰	-0.15	1951	Exp.*
Traeger <i>et al.</i> ⁵⁵	-0.09	1984	Exp.**
Lange's Handbook ²¹	-0.02	1999	Rev.
Baulch <i>et al.</i> ¹⁷	0.00	2005	Rev.
CRC ²²	0.10	2011	Rev.
3 rd Millennium ³	-0.01	2012	
Goldsmith <i>et al.</i> ⁴	-0.00 ± 0.10	2012	Calc.†
ATcT ²	-0.07 ± 0.11	2012	Calc.‡
Verevkin ⁵	-0.14	2013	Rev.
<i>Standard Deviation</i> 0.06			
Recommendation -0.06			
GA	-0.05		
* CALORIMETRY	** PMS		
† QCISDT	‡ TN		

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

Literature	S^\ominus	Year	Source
Lange's Handbook ²¹	73.04	1999	Rev.
Baulch <i>et al.</i> ¹⁷	73.60	2005	Rev.
3 rd Millennium ³	72.98	2012	
Goldsmith <i>et al.</i> ⁴	73.20 ±1.50	2012	Calc.*
<i>Standard Deviation</i>	0.24		
Recommendation	73.21		
GA	73.08		

* QCISDT

TABLE XXXVI. Molar entropy (cal K⁻¹ mol⁻¹) of 1-butene.

Literature	$\Delta_f H^\ominus$	Year	Source
Prosen <i>et al.</i> ⁶⁰	-2.58	1951	Exp*
Traeger <i>et al.</i> ⁵⁵	-2.91	1984	Exp**
Lange's Handbook ²¹	-2.72	1999	Rev.
Baulch <i>et al.</i> ¹⁷	-2.70	2005	Rev.
CRC ²²	-2.725	2011	Rev.
3 rd Millennium ³	-2.67	2012	
Goldsmith <i>et al.</i> ⁴	-2.70 ±0.20	2012	Calc.†
ATcT ²	-2.67 ±0.12	2012	Calc.‡
Verevkin ⁵	-2.56	2013	Rev.
<i>Standard Deviation</i>	0.09		
Recommendation	-2.67		
GA	-2.72		

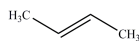
* CALORIMETRY ** PMS
† QCISDT ‡ TN

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

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.

8. 2-Butene



There is relatively good agreement within the literature for the molar entropy and heat of formation of 2-butene as shown in Tables XXXVII and XXXVIII.

The average heat of formation for 2-butene is -2.69 kcal mol⁻¹ with a standard deviation of 0.09 kcal mol⁻¹. The value from Traeger *et al.*⁵⁵ differs from the average by 0.22 kcal mol⁻¹ which is more than twice the standard and when it is excluded the average becomes -2.67 kcal mol⁻¹. The value estimated using group additivity after optimisation is -2.72 kcal mol⁻¹.

The average molar entropy of 2-butene is 70.77 cal

Literature	S^\ominus	Year	Source
Lange's Handbook ²¹	70.86	1999	Rev.
Baulch <i>et al.</i> ¹⁷	70.70	2005	Rev.
3 rd Millennium ³	70.82	2012	
Goldsmith <i>et al.</i> ⁴	70.70 ±1.50	2012	Calc.*
<i>Standard Deviation</i>	0.07		
Recommendation	70.77		
GA	70.50		

* QCISDT

TABLE XXXVIII. Molar entropy (cal K⁻¹ mol⁻¹) of 2-butene.

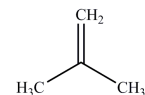
Literature	$\Delta_f H^\ominus$	Year	Source
Prosen <i>et al.</i> ⁶⁰	-4.29	1951	Exp*
Traeger <i>et al.</i> ⁵⁵	-4.04	1984	Exp**
Lange's Handbook ²¹	-4.04	1999	Rev.
Baulch <i>et al.</i> ¹⁷	-4.00	2005	Rev.
CRC ²²	-4.04	2011	Rev.
3 rd Millennium ³	-4.20	2012	
Goldsmith <i>et al.</i> ⁴	-4.10 ±0.20	2012	Calc.†
ATcT ²	-4.20 ±0.13	2012	Calc.‡
Verevkin ⁵	-4.28	2013	Rev.
<i>Standard Deviation</i>	0.11		
Recommendation	-4.16		
GA	-4.08		

* CALORIMETRY ** PMS
† QCISDT ‡ TN

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

K⁻¹ mol⁻¹ with a standard deviation of 0.07 cal K⁻¹ mol⁻¹. All of the values in Table XXXVIII 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 XXXIX.

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 XXXIX 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 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-

Literature	S^\ominus	Year	Source
Stull and Sinke ⁶¹	70.17	1969	Rev.
Frenkel <i>et al.</i> ⁶²	70.08	1984	Calc.*
Lange's Handbook ²¹	70.17	1999	Rev.
Baulch <i>et al.</i> ¹⁷	70.90	2005	Rev.
3 rd Millennium ³	68.70	2012	
Goldsmith <i>et al.</i> ⁴	70.20 ± 1.50	2012	Calc.**
<i>Standard Deviation</i> 0.66			
Recommendation 70.16			
GA 70.16			
* RRHO		** QCISDT	

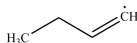
TABLE XL. Molar entropy (cal K⁻¹ mol⁻¹) of *iso*-butene.

Literature	$\Delta_f H^\ominus$	Year	Source
Baulch <i>et al.</i> ¹⁷	59.10	2005	Rev.
3 rd Millennium ³	58.76	2012	
Goldsmith <i>et al.</i> ⁴	59.30 ± 0.90	2012	Calc.*
<i>Standard Deviation</i> 0.22			
Recommendation 59.05			
GA 58.38			
* QCISDT			

TABLE XLI. Enthalpy of formation (kcal mol⁻¹) of 1-buten-1-yl radical.

sation is 70.16 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 C₄H₇ butenyl radicals. Further studies of these radicals are required.

The average of the three heat of formation values available for 1-buten-1-yl (1C₄H₇-1) radical is 59.05 kcal mol⁻¹ with a standard deviation of 0.22 kcal mol⁻¹ and all three values in Table XLI 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

Literature	S^\ominus	Year	Source
Baulch <i>et al.</i> ¹⁷	74.90	2005	Rev.
3 rd Millennium ³	74.40	2012	
Goldsmith <i>et al.</i> ⁴	74.50 ± 1.50	2012	Calc.**
<i>Standard Deviation</i> 0.16			
Recommendation 74.60			
GA 74.24			
* QCISDT			

TABLE XLII. Molar entropy (cal K⁻¹ mol⁻¹) of 1-buten-1-yl radical.

Literature	$\Delta_f H^\ominus$	Year	Source
Baulch <i>et al.</i> ¹⁷	54.20	2005	Rev.
3 rd Millennium ³	53.50	2012	
Goldsmith <i>et al.</i> ⁴	53.80 ± 0.90	2012	Calc.*
<i>Standard Deviation</i> 0.29			
Recommendation 53.83			
GA 52.14			
* QCISDT			

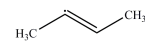
TABLE XLIII. Enthalpy of formation (kcal mol⁻¹) of 2-buten-2-yl radical.

Literature	S^\ominus	Year	Source
Baulch <i>et al.</i> ¹⁷	74.90	2005	Rev.
3 rd Millennium ³	74.40	2012	
Goldsmith <i>et al.</i> ⁴	74.50 ± 1.50	2012	Calc.**
<i>Standard Deviation</i> 1.02			
Recommendation 73.92			
GA 73.18			
* QCISDT			

TABLE XLIV. Molar entropy (cal K⁻¹ mol⁻¹) of 2-buten-2-yl radical.

standard deviation of 0.16 cal K⁻¹ mol⁻¹ and all three values in Table XLII 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.

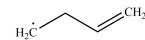
11. 2-Buten-2-yl radical



Values in the literature for the heat of formation for 2-buten-2-yl (2C₄H₇-2) radical range from 53.50³ to 54.20¹⁷ 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 (3C₄H₇-1) 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

Literature	$\Delta_f H^\ominus$	Year	Source
Baulch <i>et al.</i> ¹⁷	51.30	2005	Rev.
3 rd Millennium ³	48.90	2012	
Goldsmith <i>et al.</i> ⁴	49.80±0.90	2012	Calc.**
<i>Standard Deviation</i> 0.99			
Recommendation 50.00			
GA	49.00		

* QCISDT

TABLE XLV. Enthalpy of formation (kcal mol⁻¹) of but-3-en-1-yl radical.

Literature	S^\ominus	Year	Source
Baulch <i>et al.</i> ¹⁷	75.60	2005	Rev.
Miyoshi <i>et al.</i> ⁶³	76.72	2010	Calc.*
3 rd Millennium ³	75.85	2012	
Goldsmith <i>et al.</i> ⁴	75.50±1.40	2012	Calc.*
<i>Standard Deviation</i> 0.45			
Recommendation 75.92			
GA	76.39		

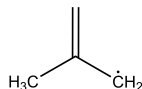
* B3LYP

** QCISDT

TABLE XLVI. Molar entropy (cal K⁻¹ mol⁻¹) of but-3-en-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 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 C₄H₇ 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 further 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 3rdMillennium database and the study by Goldsmith *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.

Literature	$\Delta_f H^\ominus$	Year	Source
Trenwith and Wrigley ⁶⁴	30.00	1977	Exp*
McMillen and Golden ³⁶	28.56	1982	Rev.
Traeger ⁶⁵	35.44	1986	Exp**
Traeger ⁶⁶	30.04	1989	Exp**
Lau <i>et al.</i> ⁶⁷	34.20±0.96	2007	Calc.†
Agapito <i>et al.</i> ⁶⁸	34.18±0.96	2007	Calc.†
3 rd Millennium ³	32.89	2012	
Goldsmith <i>et al.</i> ⁴	33.30±0.90	2012	Calc.†
<i>Standard Deviation</i> 2.31			
Recommendation 32.33			
GA	31.72		

* EI

* PI

† CCSD(T)/CBS

‡ QCISDT

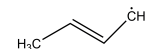
TABLE XLVII. Enthalpy of formation (kcal mol⁻¹) of 2-methylallyl radical.

Literature	S^\ominus	Year	Source
3 rd Millennium ³	71.79	2012	
Goldsmith <i>et al.</i> ⁴	70.20±1.30	2012	Calc.*
<i>Standard Deviation</i> 0.84			
Recommendation 71.05			
GA	70.57		

* QCISDT

TABLE XLVIII. Molar entropy (cal K⁻¹ mol⁻¹) of 2-methylallyl radical.

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.

Literature	$\Delta_f H^\ominus$	Year	Source
McMillen and Golden ³⁶	30.40	1982	Rev.
Traeger ⁶⁶	35.30	1989	Exp*
Baulch <i>et al.</i> ¹⁷	33.40	2005	Rev.
Lau <i>et al.</i> ⁶⁷	33.10±0.96	2007	Calc.**
Agapito <i>et al.</i> ⁶⁸	33.94±0.96	2007	Calc.**
3 rd Millennium ³	32.53	2012	
Goldsmith <i>et al.</i> ⁴	32.90±0.90	2012	Calc.†
<i>Standard Deviation</i> 1.38			
Recommendation 33.08			
GA	33.09		

* PI

** CCSD(T)/CBS

† QCISDT

TABLE XLIX. Enthalpy of formation (kcal mol⁻¹) of 1-methylallyl radical.

Literature	S^\ominus	Year	Source
Baulch <i>et al.</i> ¹⁷	68.90	2005	Rev.
3 rd Millennium ³	73.16	2012	
Goldsmith <i>et al.</i> ⁴	72.00±0.90	2012	Calc.*
<i>Standard Deviation 1.80</i>			
Recommendation 71.35			
GA	<i>70.91</i>		

* QCISDT

TABLE L. Molar entropy (cal K⁻¹ mol⁻¹) of 1-methylallyl radical.

Literature	$\Delta_f H^\ominus$	Year	Source
Chao <i>et al.</i> ⁶⁹	-56.15	1984	Calc.*
Gurvich <i>et al.</i> ⁷⁰	-56.12	1990	Rev.
Lange's Handbook ²¹	-56.12	1999	Rev.
Baulch <i>et al.</i> ¹⁷	-56.20	2005	Rev.
Matus <i>et al.</i> ⁷¹	-56.40	2006	Calc.**
CRC ²²	-56.12	2011	Rev.
NIST ¹	-56.00	2012	†
3 rd Millennium ³	-56.15	2012	
Goldsmith <i>et al.</i> ⁴	56.40 ±0.40	2012	Calc.‡
ATcT ²	-56.07±0.05	2012	Calc.§
Verevkin ⁵	-56.24	2013	Rev.
<i>Standard Deviation 0.12</i>			
Recommendation -56.19			
GA	<i>-56.13</i>		

* RRHO

** CCSD(T)

† AVG 9 MEASUREMENTS⁷²⁻⁷⁸

‡ QCISDT

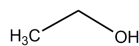
§ TN

TABLE LI. Enthalpy of formation (kcal mol⁻¹) of ethanol.

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 -56.19 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.

Literature	S^\ominus	Year	Source
Gurvich <i>et al.</i> ⁷⁰	67.30	1990	Rev.
Lange's Handbook ²¹	67.64	1999	Rev.
Baulch <i>et al.</i> ¹⁷	67.10	2005	Rev.
CRC ²²	67.30	2011	Rev.
3 rd Millennium ³	67.06	2012	
Goldsmith <i>et al.</i> ⁴	66.80 ±0.90	2012	Calc.*
<i>Standard Deviation 0.26</i>			
Recommendation 67.20			
GA	<i>67.35</i>		

* QCISDT

TABLE LII. Molar entropy (cal K⁻¹ mol⁻¹) of formation of ethanol.

Literature	$\Delta_f H^\ominus$	Year	Source
Ellison <i>et al.</i> ⁴⁹	-6.00 ±2.0	1982	Exp*
McMillen and Golden ³⁶	-4.10	1982	Rev.
Curtiss <i>et al.</i> ⁸⁰	-3.10	1995	Calc.**
Yamada <i>et al.</i> ⁸¹	-1.70	1999	Calc.†
Ervin and De Turi ⁸²	-3.60	2002	Rev.
Rauk <i>et al.</i> ⁸³	-2.37	2003	Calc.‡
Baulch <i>et al.</i> ¹⁷	-3.60	2005	Rev.
Ruscic <i>et al.</i> ⁸⁴	-3.25±0.96	2005	Rev.
Matus <i>et al.</i> ⁷¹	-2.70 ±0.98	2006	Calc.§
DeYonker <i>et al.</i> ⁸⁵	-2.60	2006	Calc.∥
3 rd Millennium ³	-2.74	2012	
Goldsmith <i>et al.</i> ⁴	-3.10 ±0.40	2012	Calc.¶
<i>Standard Deviation 1.01</i>			
Recommendation -3.01			
GA	<i>-3.31</i>		

* PES

** G2

† CBS-Q AND G2

‡ CBS-Q AND B3LYP

§ CCSD(T)

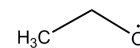
∥ ccCA

¶ QCISDT

TABLE LIII. Enthalpy of formation (kcal mol⁻¹) of ethoxy radical.

The average molar entropy for ethanol is 67.20 cal K⁻¹ mol⁻¹ with a standard deviation of 0.26 cal K⁻¹ mol⁻¹. All of the values in Table LII agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is 67.35 cal K⁻¹ 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 of heat of formation of the ethoxy radical is -3.24 kcal mol⁻¹ with a standard deviation of 1.01 kcal

Literature	S^\ominus	Year	Source
Rauk <i>et al.</i> ⁸³	66.66	2003	Calc.*
Baulch <i>et al.</i> ¹⁷	65.60	2005	Rev.
Ruscic <i>et al.</i> ⁸⁴	66.36 ± 0.96	2005	Rev.
3 rd Millennium ³	65.15	2012	
Goldsmith <i>et al.</i> ⁴	66.80 ± 1.0	2012	Calc.**
<i>Standard Deviation</i>	0.64		
Recommendation	66.11		
GA	65.64		

* CBS-Q AND B3LYP ** QCISDT

TABLE LIV. Molar entropy (cal K⁻¹ mol⁻¹) of ethoxy radical.

Literature	$\Delta_f H^\ominus$	Year	Source
Alfassi and Golden ⁸⁶	-15.20 ± 1.0	1972	Exp*
Holmes ⁸⁷	-14.50	1991	Exp**
Ruscic and Berkowitz ⁸⁸	13.70 ± 0.96	2005	Rev.
Curtiss <i>et al.</i> ⁸⁰	-12.90	1995	Calc.†
Dyke <i>et al.</i> ⁸⁹	13.60	2003	Exp.‡
Baulch <i>et al.</i> ¹⁷	-11.30	2005	Rev.
Matus <i>et al.</i> ⁷¹	-13.10 ± 0.98	2006	Calc.§
3 rd Millennium ³	-13.21	2012	
Goldsmith <i>et al.</i> ⁴	-13.00 ± 0.30	2012	Calc.
<i>Standard Deviation</i>	0.85		
Recommendation	-13.65		
GA	-13.15		

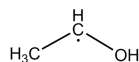
* KINETICS ** MEI
† G2 ‡ UPS
§ CCSD(T) || QCISDT

TABLE LV. Enthalpy of formation (kcal mol⁻¹) of 1-hydroxy ethyl radical.

mol⁻¹. The 1982 study by Ellison *et al.*⁷⁹ reported a value which differs from the average by ≈ 3 kcal mol⁻¹ which is more than twice the standard deviation. When that value is excluded the average becomes -3.01 kcal mol⁻¹. The value estimated using group additivity after optimisation is -3.31 kcal mol⁻¹.

The average molar entropy of the ethoxy radical is 66.11 cal K⁻¹ mol⁻¹ with a standard deviation of 0.64 cal K⁻¹ mol⁻¹. All of the values in Table LIV agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is 65.63 cal K⁻¹ mol⁻¹.

3. 1-hydroxy ethyl radical



Data for the heat of formation for the 1-hydroxy ethyl radical where the radical is located on the carbon in the α position relative to the hydroxyl group are in the range of -15.20 to -11.30 kcal mol⁻¹, Table LV. As shown in Tables LVI the number of studies that reported values for the molar entropy is limited.

The average of heat of formation for the 1-hydroxy

Literature	S^\ominus	Year	Source
Baulch <i>et al.</i> ¹⁷	67.10	2005	Rev.
3 rd Millennium ³	67.10	2012	Calc.§
Goldsmith <i>et al.</i> ⁴	68.10 ± 0.90	2012	Calc. §
<i>Standard Deviation</i>	0.80		
Recommendation	68.09		
GA	67.89		

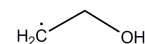
* KINETICS ** MEI
** CBS † QCISDT

TABLE LVI. Molar entropy (cal K⁻¹ mol⁻¹) of 1-hydroxy ethyl radical.

ethyl radical is -13.39 kcal mol⁻¹ with a standard deviation of 0.85 kcal mol⁻¹. The recommendation from Baulch *et al.*¹⁷ 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

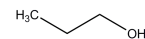


2-hydroxy ethyl radical is the ethanol radical where the radical is located on the carbon β to the hydroxyl group. While there are several studies that report heat of formation values (Table LVII), very few studies report values for the standard molar entropy of the 2-hydroxy ethyl radical (Table LVIII).

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 Holmes⁸⁷ differs from the average by ≈ 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-

Literature	$\Delta_f H^\circ$	Year	Source
Sosa and Schlegel ⁹⁰	-7.50	1991	Calc.*
Holmes ⁸⁷	-13.50±3	1991	Exp**
Yamada <i>et al.</i> ⁸¹	-8.00	2005	Rev.
Rusic and Berkowitz ⁸⁸	-8.70±2	2005	Rev.
Curtiss <i>et al.</i> ⁸⁰	-5.90	1995	Calc.†
Fulle <i>et al.</i> ⁹¹	-7.50	1997	Calc.‡
Villa <i>et al.</i> ⁹²	-4.00	2003	Calc.§
Baulch <i>et al.</i> ¹⁷	-8.60	2005	Rev.
Matus <i>et al.</i> ⁷¹	-6.20 ±0.98	2006	Calc.∥
3 rd Millennium ³	-6.17	2012	
Goldsmith <i>et al.</i> ⁴	-5.90 ±0.40	2012	Calc.¶
<i>Standard Deviation</i>	2.23		
Recommendation	-6.91		
GA	-6.45		
* HF	** MEI		
† G2	‡ SLIF		
§ CBS-Q AND B3LYP	∥ CCSD(T)		
¶ QCISDT			

TABLE LVII. Enthalpy of formation (kcal mol⁻¹) of 2-hydroxy ethyl radical.

Literature	S°	Year	Source
Baulch <i>et al.</i> ¹⁷	67.10	2005	Rev.
3 rd Millennium ³	71.13	2012	
Goldsmith <i>et al.</i> ⁴	69.40 ±1.10	2012	Calc.*
<i>Standard Deviation</i>	1.65		
Recommendation	69.21		
GA	70.14		
* QCISDT			

TABLE LVIII. Molar entropy (cal K⁻¹ mol⁻¹) of 2-hydroxy ethyl radical.

ble LIX. Table LX shows that the number of studies that report values for the standard molar entropy of propanol is limited and therefore it is difficult to assign a recommendation with certainty.

The average heat of formation for *n*-propanol is -61.07 kcal mol⁻¹ with a standard deviation of 0.12 kcal

Literature	$\Delta_f H^\circ$	Year	Source
Lange's Handbook ²¹	-60.97	1999	Rev.
CRC ²²	-60.97	2011	Rev.
NIST ¹	-61.07	2012	*
3 rd Millennium ³	-60.99	2012	
Goldsmith <i>et al.</i> ⁴	-61.30 ±0.90	2012	Calc.**
Verevkin ⁵	-61.23	2013	Rev.
<i>Standard Deviation</i>	0.12		
Recommendation	-61.07		
GA	-61.13		

* AVG 7 EXP VALUES^{72–74,93–95} ** QCISDT

TABLE LIX. Enthalpy of formation (kcal mol⁻¹) of propanol.

Literature	S°	Year	Source
Chao <i>et al.</i> ⁶⁹	77.07	1984	Exp*
Lange's Handbook ²¹	77.12	1999	Rev.
CRC ²²	77.10	2011	Rev.
3 rd Millennium ³	77.29	2012	
Goldsmith <i>et al.</i> ⁴	76.30 ±1.50	2012	Calc.**
<i>Standard Deviation</i>	0.35		
Recommendation	76.98		
GA	77.00		
* RRHO	** QCISDT		

TABLE LX. Molar entropy (cal K⁻¹ mol⁻¹) of propanol.

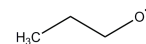
Literature	$\Delta_f H^\circ$	Year	Source
Gray <i>et al.</i> ⁹⁶	-13.00	1967	Exp*
Rauk <i>et al.</i> ⁸³	-7.00	2003	Calc.**
3 rd Millennium ³	-8.48	2012	
Goldsmith <i>et al.</i> ⁴	-8.10 ±0.90	2012	Calc.†
<i>Standard Deviation</i>	2.29		
Recommendation	-9.15		
GA	-8.31		
* KINETICS	** CBS-RAD		
† QCISDT			

TABLE LXI. Enthalpy of formation (kcal mol⁻¹) *n*-propoxy radical.

mol⁻¹. All of the values in Table LIX agree with the average within than twice the standard deviation. The value estimated using group additivity after optimisation is -61.13 kcal mol⁻¹.

The average molar entropy of *n*-propanol is 76.98 cal K⁻¹ mol⁻¹ with a standard deviation of 0.35 cal K⁻¹ mol⁻¹. All of the values in Table LX agree with the average within than twice the standard deviation. The value estimated using group additivity after optimisation is 77.00 cal K⁻¹ mol⁻¹.

6. *n*-Propoxy radical



While there is some data available for the heat of formation and molar entropy for the *n*-propoxy radical as shown in Tables LXI and LXII there is very little thermodynamic data available for the other *n*-C₃H₇O radicals and further study of these radicals is recommended.

The average heat of formation of *n*-propoxy radical is -9.15 kcal mol⁻¹ with a standard deviation of 2.29 kcal mol⁻¹. All of the values in Table LXI agree with the average within than twice the standard deviation. The value estimated using group additivity after optimisation is -8.31 kcal mol⁻¹.

The average molar entropy of *n*-propoxy radical is 74.50 cal K⁻¹ mol⁻¹ with a standard deviation of 1.41 cal K⁻¹ mol⁻¹. The three values in Table LXII agree

Literature	S°	Year	Source
Rauk <i>et al.</i> ⁸³	75.60	2003	Calc.**
3 rd Millennium ³	72.19	2012	
Goldsmith <i>et al.</i> ⁴	75.70 ±1.50	2012	Calc.†
<i>Standard Deviation</i> 1.41			
Recommendation 74.50			
GA	75.29		

** CBS-RAD

† QCISDT

TABLE LXII. Molar entropy (cal K⁻¹ mol⁻¹) of *n*-propoxy radical.

Literature	$\Delta_f H^\circ$	Year	Source
Parks <i>et al.</i> ⁹⁷	-65.20	1950	Exp*
Snelson and Skinner ⁹⁵	-65.07	1965	Exp*
Buckley and Herington ⁹⁸	-65.20	1965	Exp**
Lange's Handbook ²¹	-56.12	1999	Rev.
Sun and Bozzelli ⁹⁹	-65.19±0.31	2002	Calc.†
3 rd Millennium ³	-65.18	2012	
Goldsmith <i>et al.</i> ⁴	-65.40 ±0.30	2012	Calc.‡
ATcT ²	-65.20 ±0.09	2012	Calc.§
Verevkin ⁵	-64.91	2013	Rev.
<i>Standard Deviation</i> 0.13			
Recommendation -65.16			
GA	-65.16		

* CALORIMETRY

† CBSQ//B3

§ TN

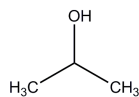
** KINETICS

‡ QCISDT

TABLE LXIII. Enthalpy of formation (kcal mol⁻¹) of *iso*-propanol.

with the average within than twice the standard deviation. The value estimated using group additivity after optimisation is 75.29 cal K⁻¹ mol⁻¹.

7. *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 than 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 than twice the standard deviation. The value estimated using group additivity after optimisation is 73.73 cal K⁻¹ mol⁻¹.

Literature	S°	Year	Source
Lange's Handbook ²¹	73.90	1999	Rev.
Sun and Bozzelli ⁹⁹	72.89	2002	Calc.*
3 rd Millennium ³	73.91	2012	
Goldsmith <i>et al.</i> ⁴	73.90 ±1.60	2012	Calc.**
<i>Standard Deviation</i> 0.50			
Recommendation 73.73			
GA	73.73		

* CBSQ//B3

‡ QCISDT

TABLE LXIV. Molar entropy (cal K⁻¹ mol⁻¹) of *iso*-propanol.

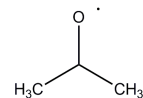
Literature	$\Delta_f H^\circ$	Year	Source
Gray <i>et al.</i> ⁹⁶	-13.00	1967	Exp*
Sun and Bozzelli ⁹⁹	-11.85	2002	Calc.**
Rauk <i>et al.</i> ⁸³	-10.00	2003	Calc.†
Goldsmith <i>et al.</i> ⁴	-10.70 ±0.90	2012	Calc.†
<i>Standard Deviation</i> 1.11			
Recommendation -11.61			
GA	-12.34		

* KINETICS

† CBS-RAD

** CBSQ//B3

‡ QCISDT

TABLE LXV. Enthalpy of formation (kcal mol⁻¹) *iso*-propoxy radical.

8. *iso*-Propoxy radical

Similar to the four *n*-C₃H₇O radicals there are only a limited number of studies that report thermodynamic data for the *iso*-C₃H₇O radicals. Tables LXV and LXVI contain values for the enthalpies of formation and molar entropies respectively.

The average heat of formation of *iso*-propoxy radical is 11.61 kcal mol⁻¹ with a standard deviation of 1.11 kcal mol⁻¹. All of the values in Table LXV agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is -12.34 kcal mol⁻¹.

The average molar entropy of *iso*-propoxy radical is 72.16 cal K⁻¹ mol⁻¹ with a standard deviation of 0.86 cal

Literature	S°	Year	Source
Sun and Bozzelli ⁹⁹	70.98	2002	Calc.*
Rauk <i>et al.</i> ⁸³	72.99	2003	Calc.**
Goldsmith <i>et al.</i> ⁴	72.16 ±1.50	2012	Calc.†
<i>Standard Deviation</i> 0.86			
Recommendation 72.16			
GA	72.02		

* CBSQ//B3

** CBS-RAD

† QCISDT

TABLE LXVI. Molar entropy (cal K⁻¹ mol⁻¹) of *iso*-propoxy radical.

Literature	$\Delta_f H^\circ$	Year	Source
Chao <i>et al.</i> ⁶⁹	–39.72	1986	Calc.*
Wiberget <i>al.</i> ¹⁰⁰	–47.80	1991	Exp**
Lange’s Handbook ²¹	–39.72	1999	Rev.
da Silva and Bozzelli ¹⁰¹	–39.72	2006	Calc.†
3 rd Millennium ³	–39.72	2012	
Verevkin <i>et al.</i> ⁵	–39.51	2013	Rev.
Goldsmith <i>et al.</i> ⁴	–39.60 ±0.10	2012	Calc.‡
<i>Standard Deviation</i>	0.39		
Recommendation	–39.65		
GA	–39.65		

* RRHO

** KINETICS

† G3, G3B3, & CBS-APNO

‡ QCISDT

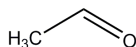
TABLE LXVII. Enthalpy of formation (kcal mol^{–1}) of ethanal.

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 thermodynamic values for aldehydes and ketones, there are very few studies that report values 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

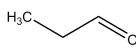


There are several studies that recommend heat of formation and molar entropy values for ethanal as shown in Tables LXVII and LXVIII below.

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 63.20 cal K^{–1} mol^{–1} with a standard deviation of 0.05 cal K^{–1} 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 Tables LXIX and LXX below.

Literature	S°	Year	Source
Lange’s Handbook ²¹	63.05	1999	Rev.
Lee and Bozzelli ¹⁰²	63.13	2006	Calc.*
CRC ²²	63.05	2011	Rev.
3 rd Millennium ³	63.09	2012	
Goldsmith <i>et al.</i> ⁴	63.00 ±0.60	2012	Calc.**
<i>Standard Deviation</i>	0.05		
Recommendation	63.20		
GA	63.07		

* CBSQ

** QCISDT

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

Literature	$\Delta_f H^\circ$	Year	Source
Tjebbes ¹⁰³	–45.76	1986	Calc.*
Buckely and Cox ¹⁰⁴	–45.90	1986	Exp**
Connett ⁹⁴	–44.46	1972	Exp**
Wiberget <i>al.</i> ¹⁰⁰	–45.09	1991	Exp**
Lange’s Handbook ²¹	–44.36	1999	Rev.
da Silva and Bozzelli ¹⁰¹	–45.18	2006	Calc.†
3 rd Millennium ³	–44.25	2012	
Verevkin <i>et al.</i> ⁵	–45.84	2013	Rev.
Goldsmith <i>et al.</i> ⁴	–45.00 ±0.90	2012	Calc.‡
<i>Standard Deviation</i>	0.58		
Recommendation	–45.07		
GA	–44.76		

* RRHO

** KINETICS

† G3, G3B3, & CBS-APNO

‡ QCISDT

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

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 1.75 cal K^{–1} mol^{–1}. All of the values in Table LXX agree with the average within twice the standard deviation. The value estimated

Literature	S°	Year	Source
Connett ⁹⁴	72.75	1972	Exp*
Lange’s Handbook ²¹	72.77	1999	Rev.
3 rd Millennium ³	69.03	2012	
Goldsmith <i>et al.</i> ⁴	73.50 ±1.3	2012	Calc.**
<i>Standard Deviation</i>	1.75		
Recommendation	72.01		
GA	71.58		

* KINETICS

** QCISDT

TABLE LXX. Molar entropy of formation (cal K^{–1} mol^{–1}) of propanal.

Literature	$\Delta_f H^\ominus$	Year	Source
Sinke and Oetting ¹¹²	-56.90	1976	Exp*
Buckley and Herington ⁹⁸	-57.05	1965	Exp**
Chao and Zwolinski ¹⁰⁷	-57.02	1976	Rev.
Lange's Handbook ²¹	-57.00	1999	Rev.
3 rd Millennium ³	-57.31	2012	
Verevkin <i>et al.</i> ⁵	-57.10	2013	Rev.
<i>Standard Deviation</i>	<i>0.14</i>		
Recommendation	-57.10		
GA	-57.23		

* CALORIMETRY ** KINETICS

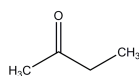
TABLE LXXV. Enthalpy of formation (kcal mol⁻¹) of butanone.

Literature	S^\ominus	Year	Source
Lange's Handbook ²¹	81.24	1999	Rev.
3 rd Millennium ³	81.27	2012	
<i>Standard Deviation</i>	<i>0.02</i>		
Recommendation	81.26		
GA	80.88		

TABLE LXXVI. Molar entropy (cal K⁻¹ mol⁻¹) of butanone.

from the 1965 study by Buckley and Herington⁹⁸ differs 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.

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 3rd 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.

Literature	$\Delta_f H^\ominus$	Year	Source
Stathis and Egerton ¹¹³	-47.80	1940	Exp*
Lay and Bozzelli <i>et al.</i> ¹¹⁴	-39.90	1997	Calc.**
Knyazev and Slagle ³⁵	-41.92	1998	Exp [†]
Chen and Bozzelli <i>et al.</i> ¹¹⁵	-44.77	2000	Calc.**
Blanksby <i>et al.</i> ¹¹⁶	-39.51	2001	Exp. [‡]
Sheng <i>et al.</i> ¹¹⁷	-39.36	2002	Calc. [‡]
Sumathi and Green ¹¹⁸	-38.79	2002	Calc. [§]
Sebbar <i>et al.</i> ¹¹⁹	-39.27	2004	Calc.
Janoshek and Rossi ¹⁰⁹	-37.98	2004	Calc. [¶]
Simmie <i>et al.</i> ¹²⁰	-39.12	2008	Calc. [‡]
3 rd Millennium ³	-38.74	2012	
Goldsmith <i>et al.</i> ⁴	-38.50 ± 0.90	2012	Calc. [#]
<i>Standard Deviation</i>	<i>2.83</i>		
Recommendation	-39.81		
GA	-38.63		

* CALORIMETRY ** MP4
[†] KINETICS [‡] CBS/APNO
[§] CBSQ ^{||} B3LYP
[¶] G3MP2B3 [#] QCISDT

TABLE LXXVII. Enthalpy of formation (kcal mol⁻¹) of ethyl hydroperoxide.

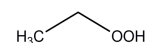
Literature	S^\ominus	Year	Source
3 rd Millennium ³	75.46	2012	
Goldsmith <i>et al.</i> ⁴	75.20 ± 1.40	2012	Calc.*
Lay <i>et al.</i> ¹²¹	76.1	1996	Calc.
<i>Standard Deviation</i>	<i>0.46</i>		
Recommendation	75.59		
GA	74.74		

* QCISDT

TABLE LXXVIII. Molar entropy (cal K⁻¹ mol⁻¹) of ethyl hydroperoxide.

E. Hydroperoxides and related radicals

1. 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 Egerton¹¹³ 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

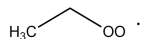
Literature	$\Delta_f H^\circ$	Year	Source
Lightfoot <i>et al.</i> ¹²²	-6.85	1992	Exp*
Knyazev and Slagle ³⁵	-6.55	1998	Exp
Blanksby <i>et al.</i> ¹¹⁶	-6.81	2001	Exp.**
Sebbar <i>et al.</i> ¹¹⁹	-5.76	2004	Calc.†
Janoshek and Rossi ¹⁰⁹	-4.90	2004	Calc.‡
Shallcross <i>et al.</i> ¹²³	-2.29	2005	Calc.§
Simmie <i>et al.</i> ¹²⁰	-5.62	2008	Calc.∥
Villano <i>et al.</i> ¹²⁴	-6.49	2011	Calc.§
3 rd Millennium ³	-6.86	2012	
Goldsmith <i>et al.</i> ⁴	-5.00 ± 0.90	2012	Calc.¶
<i>Standard Deviation</i>	1.34		
Recommendation	-6.09		
GA	-5.46		

* KINETICS ** CBS/APNO
† B3LYP ‡ G3MP2B3
∥ PM3 § CBS-QB3
¶ QCISDT

TABLE LXXIX. Enthalpy of formation (kcal mol⁻¹) of ethyl peroxy radical.

agree with the average within twice the standard deviation. The value estimated using group additivity after optimisation is 74.74 cal K⁻¹ mol⁻¹.

2. Ethyl peroxy radical

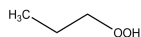


There are a number of studies that report values for the heat of formation of the ethyl peroxy radical in the literature and they show relatively good agreement as shown in Table LXXIX. Table LXXX shows that there are fewer values for the molar entropy but there is good agreement among the limited values.

The average heat of formation for the ethyl peroxy radical is -5.71 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 kcal mol⁻¹. The value estimated using group additivity after optimisation is -5.46 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

Literature	S°	Year	Source
Miyoshi <i>et al.</i> ⁶³	73.61	2010	Calc.*
Villano <i>et al.</i> ¹²⁴	74.13	2011	Calc.**
3 rd Millennium ³	73.85	2012	
Goldsmith <i>et al.</i> ⁴	74.20 ± 1.10	2012	Calc.†
<i>Standard Deviation</i>	0.23		
Recommendation	73.95		
GA	74.26		

* B3LYP ** CBS-QB3
† QCISDT

TABLE LXXX. Molar entropy (cal K⁻¹ mol⁻¹) of formation of ethyl peroxy radical.

Literature	$\Delta_f H^\circ$	Year	Source
Stathis and Egerton ¹¹³	-60.00	1940	Exp*
Chen and Bozzelliet <i>al.</i> ¹¹⁵	-44.76	2000	Calc.**
Sebbar <i>et al.</i> ¹¹⁹	-44.05	2004	Calc.†
Simmie <i>et al.</i> ¹²⁰	-44.83	2008	Calc.‡
3 rd Millennium ³	-43.41	2012	
Goldsmith <i>et al.</i> ⁴	-43.30 ± 0.90	2012	Calc.§
<i>Standard Deviation</i>	5.58		
Recommendation	-43.87		
GA	-43.63		

* CALORIMETRY ** MP4
† B3LYP ‡ CBS/APNO
§ QCISDT

TABLE LXXXI. Enthalpy of formation (kcal mol⁻¹) of *n*-propyl hydroperoxide.

n-propyl hydroperoxide available in the literature (Table LXXXII).

The average heat of formation of *n*-propyl hydroperoxide is -46.56 kcal mol⁻¹ with a standard deviation of 5.58 kcal mol⁻¹. The experimental recommendation from the 1940 study by Stathis and Egerton¹¹³ 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 kcal mol⁻¹. The value estimated using group additivity after optimisation is -43.63 kcal mol⁻¹.

The average molar entropy for *n*-propyl hydroperox-

Literature	S°	Year	Source
Simmie <i>et al.</i> ¹²⁰	83.61	2008	Calc.*
3 rd Millennium ³	87.86	2012	
Goldsmith <i>et al.</i> ⁴	84.20 ± 2.00	2012	Calc.**
<i>Standard Deviation</i>	1.88		
Recommendation	85.22		
GA	84.39		

* CBS/APNO ** QCISDT

TABLE LXXXII. Molar entropy (cal K⁻¹ mol⁻¹) of *n*-propyl hydroperoxide.

Literature	$\Delta_f H^\ominus$	Year	Source
This study**	-10.54	2013	Calc.
Villano <i>et al.</i> ¹²⁴	-11.17	2011	Calc.**
3 rd Millennium ³	-10.15	2012	
Goldsmith <i>et al.</i> ⁴	-9.80 ± 0.90	2012	Calc.†
<i>Standard Deviation</i>	0.45		
Recommendation	-10.42		
GA	-10.46		
** CBS-QB3	† QCISDT		

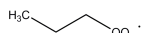
TABLE LXXXIII. Enthalpy of formation (kcal mol⁻¹) of *n*-propyl peroxy radical.

Literature	S^\ominus	Year	Source
Villano <i>et al.</i> ¹²⁴	82.80	2011	Calc.*
3 rd Millennium ³	77.64	2012	
Goldsmith <i>et al.</i> ⁴	83.50 ± 1.90	2012	Calc.**
<i>Standard Deviation</i>	2.61		
Recommendation	81.31		
GA	83.91		
* CBS-QB3	** QCISDT		

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

ide is 85.22 cal K⁻¹ mol⁻¹ with a standard deviation of 1.88 cal K⁻¹ 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 84.39 cal K⁻¹ mol⁻¹.

4. *n*-Propyl peroxy radical

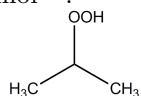


There are only a limited number of studies that report values for both the heat of formation and molar entropy of the *n*-propyl peroxy radical as shown in Tables LXXXIII and LXXXIV.

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 LXXXIII 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

Literature	$\Delta_f H^\ominus$	Year	Source
Knyazev ³⁵	-51.00	1998	Exp.*
Chen <i>et al.</i> ¹¹⁵	-48.99 ± 0.32	2000	Calc.**
Sumathi and Green ¹²⁵	-48.05	2003	Calc.**
Janoschek <i>et al.</i> ¹⁰⁹	-46.50	2003	Calc.†
Simmie <i>et al.</i> ¹²⁰	-47.90	2008	Calc.**
Goldsmith <i>et al.</i> ⁴	-47.70 ± 0.90	2012	Calc.‡
<i>Standard Deviation</i>	1.39		
Recommendation	-48.36		
GA	-47.65		
* KINETICS	** CBS		
† G3MP2B3	‡ QCISDT		

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

Literature	S^\ominus	Year	Source
Sumathi and Green ¹²⁵	81.21	2003	Calc.*
Simmie <i>et al.</i> ¹²⁰	79.97	2008	Calc.*
Goldsmith <i>et al.</i> ⁴	82.40 ± 2.1	2012	Calc.**
<i>Standard Deviation</i>	0.99		
Recommendation	81.19		
GA	80.76		
* CBS-Q	** QCISDT		

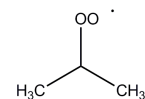
TABLE LXXXVI. Molar entropy (cal K⁻¹ mol⁻¹) of *iso*-propyl hydroperoxide.

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

Literature	$\Delta_f H^\circ$	Year	Source
Lightfoot <i>et al.</i> ¹²²	-16.47	1992	Exp*
Knyazev and Slagle ³⁵	-15.63	1998	Exp*
Janoshek and Rossi ¹⁰⁹	-14.27	2004	Calc.**
Shallcross <i>et al.</i> ¹²³	-8.79	2005	Calc.†
Simmie <i>et al.</i> ¹²⁰	-14.89	2008	Calc.‡
Villano <i>et al.</i> ¹²⁴	-15.86	2011	Calc.‡
Goldsmith <i>et al.</i> ⁴	-14.40 ± 0.90	2012	Calc.§
<i>Standard Deviation</i>	2.38		
Recommendation	-15.25		
GA	-14.48		
* KINETICS	** G3MP2B3		
† PM3	‡ CBS-QB		
§ QCISDT			

TABLE LXXXVII. Enthalpy of formation (kcal mol⁻¹) of *iso*-propyl peroxy radical.

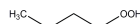
Literature	S°	Year	Source
Villano <i>et al.</i> ¹²⁴	80.97	2011	Calc.*
Goldsmith <i>et al.</i> ⁴	80.90 ± 1.90	2012	Calc.**
<i>Standard Deviation</i>	0.03		
Recommendation	80.94		
GA	80.28		
* CBS-QB	** QCISDT		

TABLE LXXXVIII. Molar entropy (cal K⁻¹ mol⁻¹) of *iso*-propyl peroxy radical.

is more than twice the standard deviation. When it is excluded the average becomes -15.25 kcal mol⁻¹. The value estimated using group additivity after optimisation is -14.48 kcal mol⁻¹.

The average of the two molar entropy values in Table LXXXVIII is 80.94 cal K⁻¹ mol⁻¹. The value estimated using group additivity after optimisation is 80.28 cal K⁻¹ mol⁻¹. Further studies are required to acquire a more accurate estimate of the uncertainty for the molar entropy of the *iso*-propyl 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.

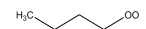
Literature	$\Delta_f H^\circ$	Year	Source
Zhu <i>et al.</i> ¹²⁶	-49.74	2007	Calc.*
Simmie <i>et al.</i> ¹²⁰	-48.37	2011	Calc.**
<i>Standard Deviation</i>	0.69		
Recommendation	-49.06		
GA	-48.63		
* CBS-QB	** PM3		

TABLE LXXXIX. Enthalpy of formation (kcal mol⁻¹) of *n*-butyl hydroperoxide.

Literature	$\Delta_f H^\circ$	Year	Source
Zhu <i>et al.</i> ¹²⁶	-17.14	2007	Calc.*
Simmie <i>et al.</i> ¹²⁰	-15.00	2011	Calc.**
Villano <i>et al.</i> ¹²⁴	-15.46	2011	Calc.*
3 rd Millennium ³	-15.18	2012	
<i>Standard Deviation</i>	0.85		
Recommendation	-15.70		
GA	-15.46		
* CBS-QB	** PM3		

TABLE XC. Enthalpy of formation (kcal mol⁻¹) of *n*-butyl peroxy radical.

8. *n*-Butyl peroxy radical



Values for the heat of formation for the *n*-butyl hydroperoxy 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 XC 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.

Literature	S°	Year	Source
Zhu <i>et al.</i> ¹²⁶	93.55	2007	Calc.*
Villano <i>et al.</i> ¹²⁴	92.43	2011	Calc.*
3 rd Millennium ³	91.19	2012	
<i>Standard Deviation</i>	0.96		
Recommendation	92.39		
GA	93.56		
* 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 XCII 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^{127,128}.

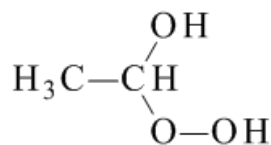


FIG. 2. Example of alcoholic hydroperoxide, CH₃CHOOH(OH).

Molecule	Source	H [°] kcal mol ⁻¹	S [°] cal mol ⁻¹ K ⁻¹	C _p cal mol ⁻¹ K ⁻¹					
				300	400	500	600	800	1000
CH ₃ CHOOH(OH)	GA 127*	-85.49	80.48	24.48	29.16	33.00	37.71	41.94	45.22
		-85.61	78.18	25.10	29.63	33.26	39.57	43.80	46.89
CH ₃ CHOO*(OH)	GA 127* 129** 128†	-50.79	80.71	22.41	26.38	29.72	33.03	37.05	40.68
		-50.62	79.32	22.39	26.39	29.81	32.63	36.97	46.89
		-50.50	83.05	21.06	25.55	29.40	32.53	37.16	40.41
CH ₃ CH ₂ CHOOH(OH)	GA 127*	-90.49	90.13	30.07	36.24	41.43	47.24	53.17	57.70
		-90.48	90.22	29.97	36.57	41.86	46.00	52.09	56.51
CH ₃ CH ₂ CHOO*(OH)	GA 127*	-55.79	90.36	28.00	33.46	38.15	42.56	48.28	53.16
		-55.75	90.13	27.78	33.18	37.84	41.73	47.77	52.25

* CBS-QB3

** G3B3

† B3LYP/CBSB7

TABLE XCII. THERM predictions of thermodynamic properties compared to calculated values for alcoholic hydroperoxide species.

IV. 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 XCIII.

Molecule	Ref	C_p cal/mol/K						
		300	400	500	600	800	1000	1500
C ₂ H ₆	GA ¹	12.44	15.48	18.48	21.24	25.68	29.18	34.70
	3	12.60	15.65	18.63	21.32	25.80	29.29	34.80
	4	12.60	15.50	18.40	21.10	25.50	29.00	34.60
C ₂ H ₅	GA	12.23	14.71	17.15	19.35	22.88	25.70	30.14
	3	12.16	14.64	17.12	19.39	22.96	25.79	30.17
	4	12.30	14.80	17.20	19.30	22.80	25.60	30.10
C ₃ H ₈	GA	18.03	22.56	26.91	30.77	36.91	41.66	49.04
	4	17.80	22.40	26.70	30.50	36.60	41.30	48.90
	11	17.67	22.47	26.91	30.76	36.99	41.73	49.21
	3	17.67	22.34	26.84	30.85	37.01	41.78	48.99
<i>n</i> C ₃ H ₇	GA	16.89	20.92	24.77	28.17	33.59	37.77	44.35
	3	15.73	19.52	23.37	26.91	32.52	36.89	43.58
	4	17.30	21.50	25.30	28.50	33.80	37.80	44.30
<i>i</i> C ₃ H ₇	GA	16.25	19.58	23.42	26.96	32.51	36.88	43.64
	3	17.12	21.14	24.95	28.33	33.53	37.59	43.91
	4	16.40	20.30	24.10	27.50	33.10	37.30	44.10
<i>n</i> C ₄ H ₁₀	GA	23.62	29.64	35.34	40.30	48.14	54.14	63.38
	4	24.00	29.70	35.20	39.90	47.70	53.70	63.10
	3	23.68	29.68	35.47	40.60	48.41	54.43	63.40
	34	23.65	29.82	35.53	40.46	48.37	54.34	63.67
<i>n</i> C ₄ H ₉	GA	22.48	28.00	33.20	37.70	44.82	50.25	58.69
	3	22.70	28.36	33.69	38.39	45.59	51.13	59.62
	4	23.00	28.50	33.60	37.90	44.90	50.20	58.60
<i>s</i> C ₄ H ₉	GA	21.84	26.66	31.85	36.49	43.74	49.36	57.98
	3	20.74	26.15	31.42	36.16	43.47	49.11	57.68
	4	21.90	27.20	32.30	36.80	44.00	49.60	58.30
<i>i</i> C ₄ H ₁₀	GA	23.56	29.95	35.73	40.67	48.39	54.20	63.41
	34	23.22	29.74	35.67	40.72	48.67	54.60	63.82
	4	23.90	30.20	35.80	40.60	48.10	53.80	63.00
<i>i</i> C ₄ H ₉	GA	23.33	29.05	34.19	38.58	45.38	50.60	58.82
	3	23.56	29.24	34.39	38.84	45.65	50.90	59.03
	4	23.10	28.90	34.00	38.30	45.10	50.30	58.60
<i>t</i> C ₄ H ₉	GA	20.75	25.76	30.89	35.57	43.06	48.84	57.89
	3	19.79	24.96	30.19	35.01	42.62	48.49	57.68
	4	21.70	26.60	31.60	36.10	43.50	49.20	58.10
C ₂ H ₄	GA	10.20	12.62	14.88	16.84	19.98	22.40	26.34
	4	10.20	12.50	14.70	16.70	19.80	22.20	26.10
	1	10.30	12.68	14.93	16.89	20.03	22.44	21.50
C ₂ H ₃	GA	10.07	11.97	13.61	15.03	17.15	18.96	21.68
	3	10.09	11.81	13.46	14.90	17.06	18.78	21.50
	4	10.40	12.30	13.90	15.20	17.40	19.70	21.80
C ₃ H ₆	GA	15.63	19.27	22.71	25.78	30.70	34.46	40.39
	4	15.40	19.10	22.60	25.60	30.50	34.20	40.20
	1	15.44	19.23	22.75	25.81	30.77	34.52	40.44
C ₃ H ₅ -s	GA	15.50	18.62	21.44	23.97	27.87	31.02	35.73
	3	15.21	18.29	21.14	23.66	27.60	30.66	35.43
	4	15.30	18.50	21.40	23.80	27.80	30.90	35.70
	130	15.39	18.93	22.01	24.64	28.79	31.90	36.79
C ₃ H ₅ -t	GA	15.23	18.19	20.98	23.60	27.77	30.98	36.21

	3	14.80	18.40	21.70	24.57	28.93	32.25	37.18
	4	15.10	18.20	21.00	23.60	27.70	30.80	35.70
	130	15.57	18.94	21.93	24.54	28.73	31.88	36.81
C ₃ H ₅ -a	GA	14.83	18.34	21.47	24.19	28.82	31.89	36.75
	3	15.22	18.99	22.28	25.04	29.06	32.12	36.74
	4	14.90	18.70	22.00	24.60	28.70	31.80	36.60
	130	15.22	18.99	22.28	25.03	29.06	32.12	36.75
C ₄ H ₈ -1	GA	20.63	25.81	30.62	34.84	41.56	46.65	54.50
	1	20.55	25.93	30.85	35.07	41.80	46.85	54.71
	3	20.55	25.40	30.13	34.46	41.39	46.61	54.37
	4	80.80	26.10	30.90	35.00	41.50	46.50	54.40
C ₄ H ₈ -2	GA	21.06	25.92	30.54	34.72	41.42	46.52	54.44
	4	21.10	26.00	30.50	34.60	41.20	46.20	54.20
	3	21.04	25.86	30.55	34.80	41.54	46.70	54.44
	1	21.04	25.94	30.61	34.76	41.53	46.66	54.65
<i>i</i> C ₄ H ₈	GA	20.97	26.17	30.99	35.16	41.73	46.74	54.53
	1	21.15	26.24	30.92	35.01	41.66	46.71	54.63
	3	20.66	26.18	31.26	35.66	42.24	47.22	54.65
	4	21.10	26.10	30.80	34.80	41.30	46.30	54.30
1C ₄ H ₇ -1	GA	20.50	25.16	29.35	33.03	38.73	43.21	49.84
	3	20.09	24.63	28.85	32.55	38.25	42.65	49.39
	1	20.55	25.93	30.85	35.07	41.80	46.85	54.71
2C ₄ H ₇ -2	GA	20.66	24.84	28.81	32.54	38.49	43.04	50.26
	3	19.96	23.86	27.86	31.58	37.53	42.14	49.15
	4	20.30	24.50	28.50	32.10	38.10	42.60	49.70
3C ₄ H ₇ -1	GA	19.49	24.17	28.48	32.24	38.24	42.76	49.81
	3	20.35	24.99	29.37	33.21	39.00	43.44	50.22
	4	20.70	25.30	29.50	33.10	38.70	43.00	49.80
C ₂ H ₅ OH	GA	15.27	18.94	22.43	25.50	30.21	33.79	39.30
	4	15.70	19.20	22.60	25.50	30.10	33.60	39.30
	1	15.65	19.41	22.89	25.87	30.57	34.10	39.68
C ₂ H ₅ O	GA	15.79	18.34	21.32	23.94	28.08	31.18	36.02
	4	15.80	18.80	21.70	24.10	28.20	31.20	36.00
	3	15.23	18.53	21.57	24.22	28.26	31.34	35.96
<i>s</i> C ₂ H ₄ OH	GA	15.05	18.07	20.89	23.34	27.30	30.29	34.73
	3	15.36	18.30	21.07	23.48	27.16	30.02	34.52
	4	15.80	18.80	21.50	23.80	27.60	30.40	34.90
<i>p</i> C ₂ H ₄ OH	GA	16.43	19.26	21.88	24.12	27.72	30.53	35.11
	3	16.39	19.34	22.04	24.37	27.92	30.69	34.99
	4	16.80	19.50	22.00	24.10	27.60	30.30	34.80
<i>n</i> C ₃ H ₇ OH	GA	20.86	26.02	30.86	35.03	41.44	46.27	53.64
	4	20.90	25.90	30.60	34.60	41.00	45.90	53.50
	1	20.54	25.82	30.64	34.75	41.26	46.12	53.76
	3	20.40	25.50	30.40	34.71	41.17	46.11	53.50
<i>n</i> C ₃ H ₇ O	GA	21.38	25.42	29.75	33.47	39.31	43.66	50.36
	3	19.61	24.48	29.05	33.06	39.10	43.68	50.50
	4	20.80	25.50	29.70	33.30	39.10	43.40	50.20
<i>i</i> C ₃ H ₇ OH	GA	21.55	26.77	31.50	35.52	41.58	46.09	53.08
	4	21.80	26.90	31.50	35.40	41.50	46.10	53.60
	1	21.45	26.80	31.54	35.45	41.36	45.64	52.28
	3	21.51	26.83	31.74	35.98	42.22	46.93	53.98
<i>i</i> C ₃ H ₇ O	GA	22.07	26.17	30.39	33.96	39.45	43.48	49.80
	4	20.80	25.60	29.70	33.30	39.00	43.20	50.00
CH ₃ O ₂ H	GA	15.71	18.89	20.96	23.32	26.43	28.82	
	131	14.79	17.35	19.67	21.65	24.78	27.21	30.72
	4	14.60	17.10	19.40	21.40	24.50	26.80	30.50
	3	16.01	18.83	21.17	23.02	25.52	27.50	30.65
CH ₃ O ₂	GA	14.54	17.11	18.68	20.58	23.18	25.14	
	3	12.52	14.64	16.76	18.67	21.54	23.70	26.92
	4	12.10	14.20	16.20	18.00	20.90	23.00	26.30
C ₂ H ₅ O ₂ H	GA	19.59	23.63	27.32	30.60	35.52	39.29	

	¹²⁷	20.42	24.09	27.44	30.32	34.95	38.48	46.50
	³	19.38	23.78	27.80	31.21	36.08	39.63	44.83
	⁴	20.00	24.10	27.80	30.80	35.60	39.20	44.80
C ₂ H ₅ O ₂	GA	18.42	21.85	25.04	27.86	32.27	35.61	
	³	18.27	22.14	25.71	28.75	33.14	36.37	
	¹²⁴	19.81	22.89	25.64	28.08	32.18	35.38	
	⁴	17.60	21.30	24.70	27.60	32.10	35.40	40.50
<i>n</i> C ₃ H ₇ O ₂ H	GA	25.18	30.71	35.75	40.13	46.75	51.77	
	¹²⁷	25.61	30.90	35.62	39.64	45.98	50.76	46.50
	³	23.36	28.81	34.06	38.65	45.35	50.39	57.95
	⁴	25.70	31.20	36.10	40.20	46.70	51.50	59.00
<i>n</i> C ₃ H ₇ O ₂	GA	24.01	28.93	33.47	37.39	43.50	48.09	
	¹²⁴	26.97	31.15	34.89	38.21	43.76	48.09	
	³	21.61	26.69	31.71	36.21	43.00	48.08	
	⁴	23.00	28.20	32.90	36.90	43.10	47.70	54.70
<i>i</i> C ₃ H ₇ O ₂ H	GA	26.39	31.85	36.67	41.00	47.02	51.70	
	¹²⁵	25.69	31.28	36.25	40.45	47.00	51.85	
	¹²⁷	26.57	32.00	36.70	40.63	46.74	51.32	46.50
	⁴	26.90	32.30	37.10	41.90	47.30	51.90	59.20
<i>i</i> C ₃ H ₇ O ₂	GA	25.22	30.07	34.39	38.26	43.77	48.02	
	¹²⁴	26.57	30.76	34.50	37.83	43.40	47.74	
	⁴	24.20	29.20	33.70	37.40	43.30	47.80	54.70
<i>n</i> C ₄ H ₉ O ₂ H	GA	30.77	37.79	44.18	49.66	57.98	64.25	
	¹²⁶	30.36	37.60	44.16	49.71	58.38	64.80	
<i>n</i> C ₄ H ₉ O ₂	GA	29.60	36.01	41.90	46.92	54.73	60.57	
	¹²⁶	27.63	34.42	40.63	45.90	54.13	60.16	
	¹²⁴	33.31	38.64	43.40	47.64	54.75	60.28	
	³	26.86	33.59	40.10	45.85	54.36	60.59	

TABLE XCIII: Specific heat capacities at constant pressure.

A. Recommended group values

Tables XCIV and XCV shows the current group values as implemented in THERM⁷ for stable and radical species respectively. The groups that underwent the largest changes are included in Table XCVI.

Group	H_f	S	C_p						
			300	400	500	600	800	1000	
C/C/H3	-10.01	30.29	6.22	7.74	9.24	10.62	12.84	14.59	
C/C2/H2	-5.00	9.65	5.59	7.08	8.43	9.53	11.23	12.48	
C/C3/H	-2.14	-11.43	4.90	6.73	8.01	8.81	9.87	10.43	
C/C4	0.10	-34.99	4.01	5.62	7.08	8.42	10.67	11.43	
CD/H2	6.28	27.59	5.10	6.31	7.44	8.42	9.99	11.20	
CD/C/H	8.65	7.83	4.31	5.22	6.03	6.74	7.87	8.67	
CD/C2	9.66	-12.27	3.43	4.38	5.07	5.50	6.06	6.36	
CD/CD/H	6.72	6.38	4.46	5.79	6.75	7.42	8.35	9.11	
C/C/H/O/OO	-16.78	-19.10	4.24	5.77	7.31	9.21	9.24	9.33	
C/C/H2/OO	-8.02	6.62	3.85	4.84	6.52	7.45	9.28	10.6	
C/C2/H/OO	-7.03	-15.46	4.43	5.32	6.63	7.23	7.94	8.47	
C/C2/O/OO	-16.36	-45.05	3.61	5.08	6.47	7.16	6.61	6.52	
C/H3/OO	-8.30	30.30	6.19	7.84	9.40	10.79	13.02	14.77	
OO/C/H	-20.60	38.64	9.52	11.05	11.56	12.53	13.40	14.05	
C/C/H2/O	-8.02	9.15	4.55	6.60	8.30	9.53	10.91	11.95	
O/C/H	-38.10	30.09	4.50	4.60	4.89	5.35	6.46	7.25	
C/C2/H/O	-7.04	-12.57	4.61	6.69	8.13	8.93	9.44	9.66	
CO/C2	-31.50	15.14	5.59	6.09	6.81	7.48	8.54	9.14	
CO/C/H	-29.34	34.45	6.72	7.71	8.77	9.90	11.45	12.63	
C/CO/H3	-10.31	30.80	6.47	8.03	9.48	10.59	12.68	14.26	
C/C/CO/H2	-5.41	9.02	5.62	6.89	8.01	9.35	10.99	12.19	

TABLE XCIV: Stable species groups as implemented by THERM.

Group	H_f	S	C_p						
			300	400	500	600	800	1000	
P	101.15	2.51	-1.14	-1.64	-2.14	-2.60	-3.32	-3.89	
IC4H9	101.60	1.64	-0.23	-0.90	-1.54	-2.09	-3.01	-3.60	
C2H5	100.77	2.27	-0.21	-0.77	-1.33	-1.89	-2.80	-3.48	
S	98.07	4.26	-1.78	-2.98	-3.49	-3.81	-4.40	-4.78	
T	96.14	5.14	-2.81	-4.19	-4.84	-5.10	-5.33	-5.36	
VIN	110.53	1.16	-0.13	-0.65	-1.27	-1.81	-2.83	-3.44	
VINS	106.96	1.31	-0.40	-1.08	-1.73	-2.18	-2.93	-3.48	
ALLYLP	87.90	-1.77	-0.80	-0.93	-1.24	-1.59	-1.88	-2.57	
ALLYL	85.50	-3.81	-1.54	-1.82	-2.08	-2.32	-2.75	-3.14	
ALKOXY	104.92	-1.71	0.52	-0.60	-1.11	-1.56	-2.13	-2.61	
CJCOH	101.78	1.99	1.16	0.32	-0.55	-1.38	-2.49	-3.26	
CCJOH	95.08	0.54	-0.22	-0.87	-1.54	-2.16	-2.91	-3.50	
ALPEROX	85.27	-0.48	-1.17	-1.78	-2.28	-2.74	-3.25	-3.68	
ALPEROXH	86.80	0.23	-2.07	-2.78	-3.28	-4.68	-4.89	-4.54	

TABLE XCV: Radical groups as implemented by THERM.

V. DISCUSSION OF GROUP ADDITIVITY OPTIMISATION

Table XCVI shows the THERM groups that express the largest differences between the new and old groups, many of the old groups originate from Benson⁶. 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 by 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 alkoxy group has increased by 0.86 cal K⁻¹ mol⁻¹. Further study of the thermodynamic properties of the C₃H₇O 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 thermochemical properties calculated theoretically^{127,128} 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.

Group		H_f	S	C_p					
				300	400	500	600	800	1000
VINS	Old	109.00	1.81	-0.34	-1.21	-1.94	-2.52	-3.34	-3.91
	New	106.96	1.31	-0.40	-1.08	-1.73	-2.18	-2.93	-3.48
	Δ	2.04	0.50	0.06	-0.13	-0.21	-0.34	-0.41	-0.43
ALKOXY	Old	104.06	-1.46	-0.98	-1.30	-1.61	-1.89	-2.38	-2.80
	New	104.92	-1.71	0.52	-0.60	-1.11	-1.56	-2.13	-2.61
	Δ	0.86	0.25	-1.50	-1.00	-0.50	-0.33	-0.25	-0.50
O/C/H	Old	-37.90	29.07	4.30	4.50	4.82	5.23	6.02	6.61
	New	-38.10	30.09	4.50	4.60	4.89	5.35	6.46	7.25
	Δ	0.20	-1.02	-0.20	-0.10	-0.07	-0.12	-0.44	-0.56
C/C2/H/OO	Old	-6.08	-11.96	4.21	5.85	7.15	8.10	9.38	10.10
	New	-7.03	-15.46	4.43	5.32	6.63	7.23	7.94	8.47
	Δ	0.95	3.50	-0.22	0.53	0.63	0.65	1.41	1.85
OO/C/H	Old	-23.50	36.84	9.74	10.47	11.00	11.74	12.19	12.91
	New	-20.60	38.64	9.52	11.05	11.56	12.53	13.40	14.05
	Δ	-2.90	-1.80	0.22	-0.58	-0.56	-0.79	-1.21	-1.14
ALPEROX	Old	86.30	0.22	-2.05	-2.84	-3.55	-4.09	-4.72	-4.97
	New	85.27	-0.48	-1.17	-1.78	-2.74	-3.25	-3.68	-3.74
	Δ	1.03	0.70	-0.88	-1.06	-0.81	-0.84	-1.04	-1.23

TABLE XCVI: Groups that have undergone the largest changes

VI. CONCLUSIONS

A thorough literature review of thermochemical properties was undertaken for C₁–C₄ 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 entropy 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 Benson⁶. 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.

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