

Thermochemical Kinetics for the Lignocellulosic Biofuel, Ethyl Levulinate

Manik Kumer Ghosh¹, Stephen Dooley¹

1. School of Physics, Trinity College Dublin, The University of Dublin, Ireland.

1. INTRODUCTION

The catalytic conversion of biomass derived cellulose, hemicellulose and lignin to platform chemicals and fuels has been widely recognised as an opportunity to produce sustainable transport fuels. Ethyl levulinate (EL) is one of many liquid phase molecules that may be easily produced by the acid hydrolysis of cellulose. It may be produced at the high yields that are essential for potential economic viability either by reaction of ethanol, the biorefinery platform chemical, levulinic acid, or by the insitu acid-catalysed reaction of cellulosic sugars with ethanol [1]. Ethyl levulinate has an energy density of 31.2 MJ/L, much superior to that of ethanol (24 MJ/L). The synthetic processes that produce ethyl levulinate from cellulose use ethanol (both as a solvent and) as a means of functionalising the levulinic acid precursor [2]. This alkylation also improves the energy density of the cellulose derived functionalities, and their solubility in conventional petroleum derived liquid hydrocarbon fuels.

The position of the fuel and combustion literature on the prospective uses of ethyl levulinate may thus be summarised as suggesting ethyl levulinate to be intermediate in physical property between gasoline and diesel distillate, but of a kinetic propensity much lower than conventional diesel, and even lower than conventional gasoline. We note that the to-date reactivity indicators are all derived from engine like configurations, where no information of a fundamental kinetic nature is available for reference. In analysing fundamentally analysing the combustion kinetics of the ethyl levulinate oxidation reaction, we have realised that there are potentially corrupting inaccuracies in the state-of-art thermochemical descriptors of ester systems. The purpose of the present contribution is to highlight this issue and share our suggestions of a standard methodology definition with which to determine and collect ("data mine") reliable and accurate thermochemical parameters for the complicated oxygenated hydrocarbons that are typical of both biofuels and low temperature combustion intermediates.

2. METHODOLOGY

This study utilises and contrasts the two methodologies principally employed to determined thermochemistry of combustion species; "chemical group additivity", "atomisation" and "isodesmic worked reactions". For the electronic structure determinations we use three methods, CBS-QB3, CBS-APNO and G4MP2. The computational methodologies we employ are as follows; The geometries of ethyl levulinate and all pertinent radicals are initially optimized with B3LYP/6-31G(d,p) level of theory. These B3LYP/6-31G(d,p) optimized geometries are then further optimized using the CBS-QB3, CBS-APNO, and G4MP2 methodologies [3, 4]. These methodologies have been frequently employed to compute gas phase thermochemistry in previous works, showing close accuracy (1 kcal/mol) to (expected) standard values [5, 6]. With the isodesmic reaction methodology, the CBS-QB3 procedure is typically thought of as delivering highly satisfactory results [7].

3. RESULTS AND DISCUSSION

Corresponding author: Dr Manik Kumer Ghosh, ghoshm@tcd.ie

Reliable formation enthalpies, ΔH_f^0 for all alkyl and alkoxy radicals of the ethyl levulinate system are key requirements for the estimation of thermochemical and kinetic quantities which can describe the ethyl levulinate oxidation mechanism. For oxygenated hydrocarbons bearing the ethyl ester or methyl ketone functionalities reliable thermochemical quantities already exist [3, 4], and are most conveniently utilised in the context of chemical group additivity. However, the thermochemical properties of the methylene groups located between the ethyl-ester and methyl-ketone moieties of ethyl levulinate present unstudied identities within the context of combustion kinetics. Consequently, it is expected that existing thermochemical group contributions available to estimate radical formation enthalpies associated with these identities are inappropriate.

The calculated enthalpies of formation of molecules and radicals specific to the ethyl levulinate oxidation mechanism, as proposed in this work by each of the various methods and electronic structure methodologies are listed in Table 1. When combined with well-known reference values for small radicals, each of these data sets produce distinct bond dissociation energies for the ethyl levulinate molecule. We use these BDEs as performance indicator for each methodology. This data is shown in Table 2. Note in most instances, each result differs by at least 1-2 kcal/mol. It can be seen that the bond dissociation energies of C–H bonds of ethyl levulinate are similarly overestimated by the employed group contributions by 0.3 – 2.8 kcal/mol, with the C–O bonds more modestly underestimated by up to 1.2 kcal/mol. CBS-QB3 has been a common method for estimating thermochemistry of oxygenated species [4, 5, 6]. These data have been assimilated into the group scheme used to produce the group additivity estimates of Table 2. These therefore show a lower deviation to the ethyl levulinate CBS-QB3 calculations, $\sim -0.1 - 1.6$ kcal/mol for C–H bonds, and $-0.9 - 0.5$ kcal/mol for C–O bonds. The case of C–C bonds is more complex as molecules bearing both ester and ketone functionalities have not been previously studied, the group contributions should therefore be of limited reliability and are shown to deviate by up to 1.4 kcal/mol to our recommended values.

Species	Isodesmic Worked Reactions				Group Additivity	Atomization
	CBS-QB3	CBS-APNO	G4MP2	Average (CBS-QB3 + CBS-APNO + G4MP2)		Average (CBS-QB3 + CBS-APNO + G4MP2)
<i>Molecules</i>						
CH ₃ C(O)CH ₂ CH ₂ C(O)OCH ₂ CH ₃	-148.6	-147.9	-147.8	-148.1 ± 0.38	-147.2	-148.8
CH ₃ C(O)CH ₂ CH ₂ C(O)OH	-145.6	-145.2	-145.1	-145.3 ± 0.23	-145.1	-145.1
CH ₃ C(O)CH ₂ CH ₂ C(O)OCH ₃	-140.5	-139.7	-139.8	-140.0 ± 0.34	-139.2	-140.8
<i>Alkyl and Alkoxy Radicals Derived From Ethyl Levulinate C–C and C–O Fission</i>						
CH ₃ C(O)CH ₂ CH ₂ Ċ(O)	-44.4	-44.1	-46.4	-45.0 ± 1.14	-43.9	-44.5
CH ₃ C(O)CH ₂ CH ₂ C(O)Ċ	-87.8	-86.5	-89.7	-88.0 ± 1.33	-87.2	-87.7
CH ₃ C(O)CH ₂ CH ₂ C(O)OĊH ₂	-92.8	-92.3	-95.9	-93.7 ± 1.62	-91.3	-94.1
Ċ(O)CH ₂ CH ₂ C(O)OCH ₂ CH ₃	-98.9	-98.0	-101.8	-99.6 ± 1.61	-98.0	-99.9
<i>Alkyl Radicals Derived From Ethyl Levulinate C–H Fission</i>						
ĊH ₂ C(O)CH ₂ CH ₂ C(O)OCH ₂ CH ₃	-105.4	-104.8	-107.9	-106.0 ± 1.37	-102.3	-106.1
CH ₃ C(O)ĊHCH ₂ C(O)OCH ₂ CH ₃	-109.4	-108.3	-111.6	-109.8 ± 1.41	-108.4	-109.9
CH ₃ C(O)CH ₂ ĊHC(O)OCH ₂ CH ₃	-106.8	-106.1	-109.2	-107.3 ± 1.37	-105.7	-107.5
CH ₃ C(O)CH ₂ CH ₂ C(O)OĊHCH ₃	-103.1	-102.3	-106.0	-103.8 ± 1.61	-101.8	-103.9
CH ₃ C(O)CH ₂ CH ₂ C(O)OCH ₂ ĊH ₂	-98.2	-97.8	-101.4	-99.1 ± 1.65	-96.6	-99.2

Table 1: Computed enthalpies of formation, ΔH_f^0 (298.15 K) (kcal/mol) for radicals and molecules of the ethyl levulinate oxidation system employing isodesmic work reactions and atomization procedures with various electronic structure theories, i.e. CBS-QB3, CBS-APNO, and G4MP2.

This apparent situation with the present art is thus very unsatisfactory. A standard computational methodology with which to determine oxygenated hydrocarbon thermochemistry is required. For the purposes of the present study on ethyl levulinate combustion kinetics, the formation enthalpies of all species of the ethyl levulinate submodel have been adjusted to the formation enthalpy recommended in Table 1.

It can be seen that the bond dissociation energies of C–H bonds of ethyl levulinate are similarly overestimated by the employed group contributions by 0.3 – 2.8 kcal/mol, with the C–O bonds more modestly underestimated by up to 1.2 kcal/mol. CBS-QB3 has been a common method for estimating thermochemistry of oxygenated species [8, 9]. These data have been assimilated into the group scheme used to produce the group additivity estimates of Table 2. These therefore show a lower deviation to the ethyl levulinate CBS-QB3 calculations, ~ –0.1 – 1.6 kcal/mol for C–H bonds, and –0.9 – 0.5 kcal/mol for C–O bonds. The case of C–C bonds is more complex as molecules bearing both ester and ketone functionalities have not been previously studied, the group contributions should therefore be of limited reliability and are shown to deviate by up to 1.4 kcal/mol to our recommended values.

Bonds	Isodesmic Worked Reactions			Average (CBS-QB3 + CBS-APNO + G4MP2)	Group Additivity
	CBS-QB3	CBS-APNO	G4MP2		
<i>C – H Bonds</i>					
H – CH ₂ C(O)CH ₂ CH ₂ C(O)OCH ₂ CH ₃	95.4	95.2	92.1	94.2	97.0
CH ₃ C(O)CH – (H)CH ₂ C(O)OCH ₂ CH ₃	91.4	91.7	88.3	90.5	90.9
CH ₃ C(O)CH ₂ CH – (H)C(O)OCH ₂ CH ₃	94.0	94.0	90.5	92.9	93.6
CH ₃ C(O)CH ₂ CH ₂ C(O)OCH – (H)CH ₃	97.6	97.7	94.0	96.4	97.5
CH ₃ C(O)CH ₂ CH ₂ C(O)OCH ₂ CH ₂ – H	102.5	102.3	98.6	101.1	102.8
<i>C – C Bonds</i>					
CH ₃ – C(O)CH ₂ CH ₂ C(O)OCH ₂ CH ₃	84.7	84.9	81.1	83.6	84.0
CH ₃ C(O) – CH ₂ CH ₂ C(O)OCH ₂ CH ₃	83.6	83.2	81.1	82.6	82.2
CH ₃ C(O)CH ₂ – CH ₂ C(O)OCH ₂ CH ₃	79.8	80.1	77.7	79.2	79.9
CH ₃ C(O)CH ₂ CH ₂ – C(O)OCH ₂ CH ₃	93.7	93.5	90.8	92.7	95.2
CH ₃ C(O)CH ₂ CH ₂ C(O)OCH ₂ – CH ₃	90.8	90.6	86.9	89.5	90.8
<i>C – O Bonds</i>					
CH ₃ C(O)CH ₂ CH ₂ C(O) – OCH ₂ CH ₃	101.3	100.9	98.5	100.2	99.0
CH ₃ C(O)CH ₂ CH ₂ C(O)O – CH ₂ CH ₃	89.5	90.0	86.8	88.8	88.6

Table 2: Bond dissociation energies (298.15 K) (kcal/mol) of ethyl levulinate at CBS-QB3, CBS-APNO, and G4MP2 levels of theory using the isodesmic worked reaction methodology and group additivity contributions.

This apparent situation with the present art is thus very unsatisfactory. A standard computational methodology with which to determine oxygenated hydrocarbon thermochemistry is required. For the purposes of the present study on ethyl levulinate combustion kinetics, the formation enthalpies of all species of the ethyl levulinate submodel have been adjusted to the formation enthalpy recommended in Table 1. Simmie and Sommers also noted this issue in their works on a benchmark series of small molecules [5] and radicals [6], noting that the unweighted averaging of CBS-APNO/G3/G4 results in better than 0.1 kcal/mol reproduction of their selected benchmark data. Following Simmie and Sommers, we show in this presentation that the unweighting averaging of the results of CBS-QB3/CBS-APNO/G4MP2 can produce a root mean squared deviation from a carefully chosen reference set of formation enthalpies of 0.4 kcal/mol for radical species and 0.5 kcal/mol for neutral species for the atomization methodology. The isodesmic reaction methodology require more

work, but is expected to be more accurate for larger molecules. In this presentation we establish what this accuracy is likely to be and use the comparison to foster a community discussion on the standardised determination of accurate combustion thermochemistry.

3. CONCLUSION

The bond dissociation energies for the ethyl levulinate molecule have been determined through a series of isodesmic reactions that computed the enthalpy of reaction and thereby the enthalpy of formation at CBS-QB3, CBS-APNO, and G4MP2 level of theories. The current calculations reveal that the use of one computational method is not appropriate to determining combustion thermochemical properties. However, we show that the averaging of the results of CBS-QB3, CBS-APNO and G4MP2 does deliver highly satisfactory results for both neutral and radical species typical of oxygenated hydrocarbon combustion, even with the atomization procedure.

REFERENCES

- [1] M. Mascal, E.B. Nikitin, *Green Chemistry* 12 (2010) 370-373.
- [2] T. Flannelly, S. Dooley, J.J. Leahy, *Energy & Fuels* 29 (2015) 7554-7565.
- [3] J.A. Montgomery Jr, M.J. Frisch, J.W. Ochterski, G.A. Petersson, *The Journal of chemical physics* 110 (1999) 2822-2827.
- [4] J.A. Montgomery Jr, M.J. Frisch, J.W. Ochterski, G.A. Petersson, *The Journal of Chemical Physics* 112 (2000) 6532-6542.
- [5] J.M. Simmie, K.P. Somers, *The Journal of Physical Chemistry A* 119 (2015) 7235-7246.
- [6] K.P. Somers, J.M. Simmie, *The Journal of Physical Chemistry A* 119 (2015) 8922-8933.
- [7] J.M. Simmie, G. Black, H.J. Curran, J.P. Hinde, *The Journal of Physical Chemistry A* 112 (2008) 5010-5016.
- [8] A.M. El-Nahas, M.V. Navarro, J.M. Simmie, J.W. Bozzelli, H.J. Curran, S. Dooley, W. Metcalfe, *Enthalpies of Formation, The Journal of Physical Chemistry A* 111 (2007) 3727-3739.
- [9] J.M. Hudzik, J.W. Bozzelli, *J Phys Chem A* 116 (2012) 5707-5722.