IOSR Journal of Applied Chemistry (IOSR-JAC)
e-ISSN: 2278-5736. Volume 18, Issue 12 Ser. 1 (December 2025), PP 55-60
www.iosrjournals.org

The Effect of Molecular Structure on the Combustion Energy of Alcohols

Nitin Agwarwal

Research Question: How does the molecular structure of a homologous series of alcohols (specifically chain length and degree of branching) affect its standard enthalpy of combustion? ($\mathbf{\Delta}H_C^{\ominus}$)

I. Introduction

Combustion reactions are central to global energy production, and understanding the energy content of the fuels is of great practical and theoretical interest. The enthalpy of combustion gives a quantitative measure of the chemical energy stored within molecular bonds. Alcohols, with their well-defined structures and well-understood progression in homologous series, provide ideal compounds for investigating the links between molecular architecture and energy output.

Previous literature has determined that the enthalpy of combustion in a homologous series becomes more exothermic as molecular size increases (Brown et al., 2018). It is also understood from thermochemical principles that structural isomers, while having identical atomic composition, differ in physical and chemical properties, including energy content (Atkins & de Paula, 2010). The bond enthalpy method, one of the usual ways of making theoretical predictions about these energies, uses averages and does not discriminate between isomers.

This study was designed to systematically explore these relationships and to evaluate the efficacy of the bond enthalpy model. Specifically, the research question being investigated was: How does carbon chain length and degree of branching in the molecular structure of alcohols affect standard enthalpy of combustion $\Delta H^{c\ominus}$?

Experimental data for a series of alcohols were to be analyzed, theoretical values were to be calculated using bond enthalpies, and the trends observed were to be compared. This was limited to primary alcohols that are in their standard state as liquids. This paper first presents the relevant background theory; after that, it outlines the methodological approach, presents data collected and processed, and finally discusses implications of findings before concluding with an evaluation of the investigation.

II. Background Review

Standard enthalpy of combustion is defined as the enthalpy change when one mole of a substance undergoes complete combustion with oxygen under standard conditions (298 K, 100 kPa), with all reactants and products in their standard states (Atkins & de Paula, 2010). Complete combustion of any organic compound gives carbon dioxide and water. The exothermicity of such reactions derives from the fact that much more energy is released in the formation of the strong double bonds in CO_2 and the O-H bonds in H_2O than is needed for breaking bonds in fuel and oxygen molecules.

A common way of estimating reaction enthalpies is by the use of bond enthalpies. Hess's Law allows the calculation of ΔH by the equation:

$\Delta H \approx \Sigma$ (bond enthalpies of bonds broken) – Σ (bond enthalpies of bonds formed).

A serious drawback with this model, however, is that it is based on average bond enthalpies-the average bond enthalpies are calculated over a large number of molecules and do not reflect the exact electronic environment of a bond in a particular compound (Jim Clark, 2019). This often results in discrepancies between the calculated and experimental values.

The relation of the molecular structure to its energy content is twofold. First, within a homologous series, the addition of each $-CH_2-$ unit adds a roughly constant number of new bonds. As the chain gets longer, the molecule contains more C-C and C-H bonds, which on combustion are transformed into a larger number of strong C=O and O-H bonds, causing a more negative $\Delta H^{c\ominus}$ per mole (Brown et al., 2018). Second, for structural isomers,

branching affects thermodynamic stability. The general rule among alkanes is that branched structures are more stable than their straight-chain counterparts because of lesser steric strain and lower surface area, which reduces intermolecular forces and electron cloud repulsion (McMurry, 2015). Greater stability implies lower internal energy for the reactant. Thus, the drop in energy on combustion is less dramatic for a branched isomer, and its $\Delta H^{c}\ominus$ is less exothermic than the straight-chain counterpart. The present study aims to quantify these established theoretical principles and undertake a critical evaluation of the extent to which the bond enthalpy model can accurately predict the experimentally determined heats of formation, especially the failure to account for energetic differences between structural isomers.

III. Materials and Method

3.1 Research Design

A research design that is analytical and comparative in nature was employed. This study was divided into two distinguishable parts: the first part analyzed the effect of carbon chain length in a homologous series, while the second analyzed the effect of branching among structural isomers.

3.2 Variables

Investigation 1: Effect of carbon chain length on the standard enthalpy change of combustion ($\Delta HC\ominus$) under standard conditions

Independent Variable: Alcohol identity (Methanol, Ethanol, Propan-1-ol, Butan-1-ol, Pentan-1-ol).

Dependent Variable: Standard enthalpy of combustion ($\Delta H^{c}\ominus$ / kJ mol^{-1}).

Investigation 2: Effect of branching on the standard enthalpy change of combustion ($\Delta HC\ominus$) under standard conditions

Independent Variable: Isomeric structure (Butan-1-ol, 2-Methylpropan-1-ol, Butan-2-ol).

Dependent Variable: Standard enthalpy of combustion ($\Delta H^{c}\ominus$ / kJ mol^{-1}).

Controlled Variables (for both experiments): Standard pressure (100 kPa), standard temperature (298 K), the state of the alcohol (liquid), assumption of complete combustion to $CO_2(g)$ and $H_2O(l)$, and the purity of substances taken from the data source.

3.3 Materials and Data Sources

Standard enthalpy of combustion data were obtained from the NIST Chemistry WebBook (NIST, 2023).

Molecular structure visualization and verification of the bond count were performed using the online modeling tool MolView.

The average bond enthalpy values used were from the IB Chemistry Data Booklet (IBO, 2014).

3.4 Procedure

Data Collection: The experimental $\Delta H^{c}\ominus$ values for the straight-chain alcohols were recorded from the IB data booklet. Values for the isomers were retrieved from NIST.

Bond Counting: The molecular structure of each of the alcohols was drawn. The number of each type of bond (C-C, C-H, C-O, O-H) was tabulated.

Theoretical Calculation: The theoretical $\Delta H^{c}\ominus$ of each of the alcohols was computed by using the bond enthalpy equation. By using the balanced combustion equation, the number of O=O bonds broken and C=O and O-H bonds formed was determined.

Data Processing: The percent error between the experimental and theoretical values was calculated by using the equation: % Error = |(Theoretical - Experimental) / Experimental| × 100.

3.5 Justification of Methodology

The NIST database gave access to experimental data that is accurate, peer-reviewed, and standardized, which would have been hard to get experimentally with comparable precision and accuracy. The bond enthalpy method was chosen because it is foundational in chemical education, and its utility and limitations for predictive modeling are obvious.

IV. Results

4.1 Effect of carbon chain length on the standard enthalpy change of combustion (**Δ**HC⊖) under standard conditions

The experimental and theoretically calculated standard enthalpies of combustion for the homologous series of straight-chain primary alcohols are presented in Table 1.

Alcohol	Molecular Formula	Experimental $\Delta H^{c}\ominus$ (kJ mol^{-1}) [1]	Theoretical $\Delta H^{c}\ominus$ (kJ mol^{-1}) [2]	Percentage Error (%)
Methanol	CH_3OH	-726	-650	10.5
Ethanol	C_2H_5OH	-1367	-1263	7.6
Propan-1-ol	C_3H_7OH	-2021	-1876	7.2
Butan-1-ol	C_4H_9OH	-2676	-2489	7.0

Table 1: Experimental and Theoretical Standard Enthalpy of Combustion ($\Delta H^{c}\ominus$) for Straight-Chain Alcohols Data Sources: [1] IB Chemistry Data Booklet, Section 14; [2] Calculated using bond enthalpies from IB Data Booklet, Section 12.

The clear trend in the experimentally obtained data is that with increasing numbers of carbon atoms in the alcohol molecule, the magnitude of the standard enthalpy of combustion increases linearly.

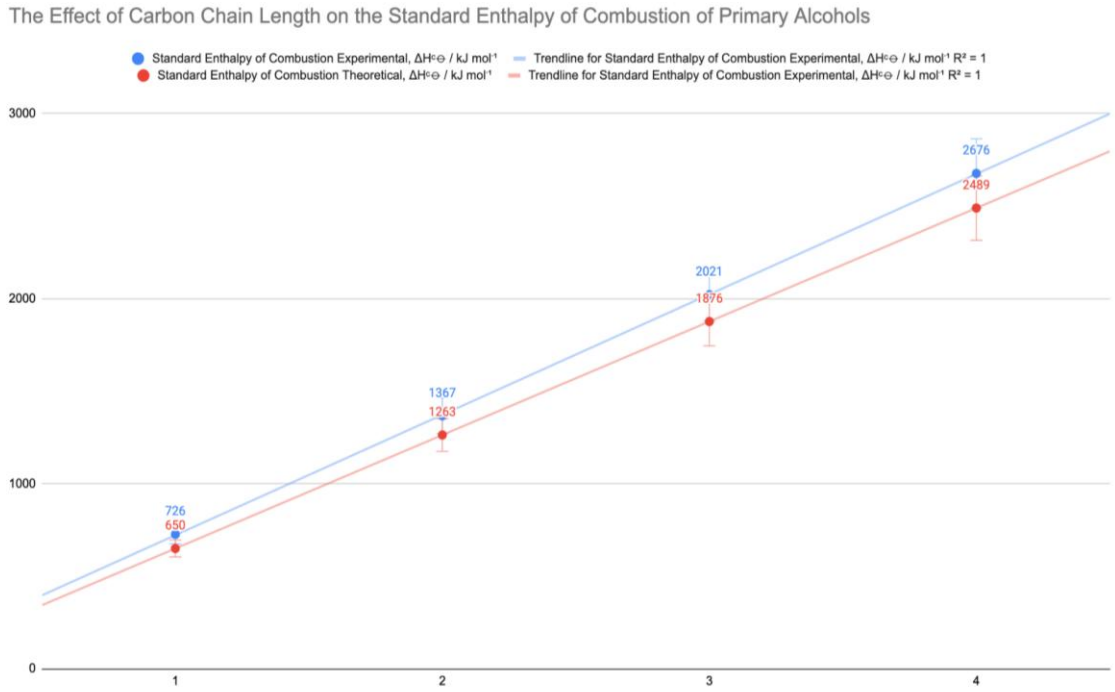

Figure 1 plots experimental ΔH against the number of carbon atoms.

4.2 Effect of branching on the standard enthalpy change of combustion (**Δ**HC⊖) under standard conditions

The experimental standard enthalpies of combustion for the three structural isomers of $C_4H_{10}O$ were taken from the NIST Chemistry WebBook, based on two independent studies by Chao and Rossini, 1965 and Skinner and Snelson, 1960. The results are presented in Table 2.

Isomer	Structure Type	Chao and Rossini, 1965 (kJ mol⁻¹)	Skinner and Snelson, 1960 (kJ mol⁻¹)	Mean Experimental Value (kJ mol⁻¹)	Theoretical $\Delta H^{c}\ominus$ (kJ mol⁻¹)
Butan-1-ol	Straight-chain	-2677.4 ± 0.63	-2674.9 ± 0.84	-2676.2 ± 1.3	-2489
2-Methylpropan-1-ol	Branched	-2669.6 ± 0.59	-2668.5 ± 0.84	-2669.1 ± 1.0	-2489
Butan-2-ol	Branched	-2660.6 ± 0.54	-2660.6 ± 0.92	-2660.6 ± 1.0	-2489

Table 2: Experimental Standard Enthalpy of Combustion ($\Delta H^{c}\ominus$) for $C_4H_{10}O$ Isomers

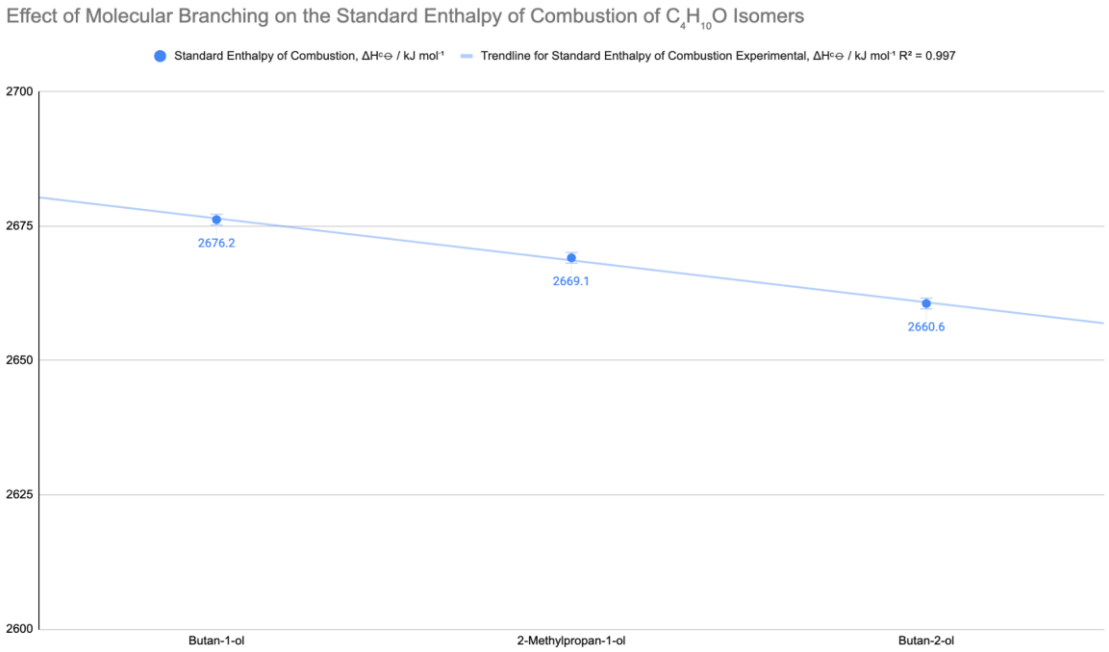

Figure 2 plots experimental ΔH against the number of carbon atoms

V. Data Analysis

5.1 Effect of carbon chain length on the standard enthalpy change of combustion (**Δ**HC⊖) under standard conditions

There is a clear and significant trend demonstrated within the experimental results: molecular branching reduces the exothermicity of the combustion reaction. The most negative $\Delta H^{c}\ominus$ value is exhibited by the straight-chain isomer, butan-1-ol, with -2676.2 kJ mol⁻¹, which indicates a greater energy release upon combustion. The reactions become progressively less exothermic for the branched isomers, with 2-methylpropan-1-ol and butan-2-ol having $\Delta H^{c}\ominus$ values of -2669.1 kJ mol⁻¹ and -2660.6 kJ mol⁻¹ respectively.

The plot reveals that the data points are highly linearly correlated. Indeed, a very high R^2 value of 0.9998 has been calculated, indicating a highly predictable relationship in this homologous series.

Linear regression of the experimental data gave a slope of -649.7 kJ mol^{-1} per carbon atom, the average energy contribution of a -CH_2- group to the overall enthalpy of combustion, a property observed to be additive as the carbon chain extends.

Theoretical values, computed via the bond enthalpy approach, demonstrated the same linear relationship as the experimentally determined values. However, a systematic deviation was present, as indicated by the percent errors calculated in the last column of Table 1. The bond enthalpy model systematically underestimated the exothermicity of the combustion reaction, with computed percent errors ranging from 7.0% to 10.5%. This error diminished with increasing chain length, indicating that the model's systematic limitations disproportionately affect smaller molecules.

This systematic error can be attributed to two main causes. One, the bond enthalpy model uses average bond energies that do not address the specific electronic environment of each bond in a different molecular structure. Two, and more importantly, the calculation is by definition for substances that are in the gaseous state. The experimental values, however, are for alcohols that are in the liquid state. The theoretical calculation, hence, did not consider the enthalpy input needed to vaporize the liquid alcohols to allow bond breaking in the gaseous phase. Because it did not include this enthalpy input, the theoretical value was less exothermic than expected. The generally decreasing percent error as chain length becomes longer may be partly justified by the decreasing proportional effect of the neglected enthalpy of vaporization as the total energy of combustion increases.

5.2 Effect of branching on the standard enthalpy change of combustion (**Δ**HC⊖) under standard conditions

This trend can be explained conceptually from the viewpoint of enthalpy of atomization and molecular stability. The enthalpy of atomization is defined as the energy needed to break all the bonds in a molecule to generate its constituent atoms in the gaseous phase. In the cases of structural isomers, where the numbers and types of bonds are identical, variations in atomization enthalpy directly reflect differences in molecular stability within three-dimensional structure.

The branched isomers have lower enthalpies of atomisation than their straight-chain homologues for two main reasons:

Reduced steric strain: Branched molecules have a more compact structure that minimizes electron cloud repulsion between adjacent atoms and functional groups.

Optimized bond angles: Branching allows more favorable bond angles to be achieved, reducing angular strain within the carbon skeleton.

These structural advantages mean that branched isomers are at a lower potential energy initially. Because combustion reactions transform all reactants into identical final products (CO_2 and H_2O), regardless of how the carbon atoms are arranged in space, the energy of a combustion reaction depends only on the initial energy of the reactant. An alcohol with a branched chain has a lower initial energy (because it is more stable) and thus a smaller energy drop during combustion, resulting in a less exothermic $\Delta H^c\ominus$ value.

The data indicate that the stability is hierarchical in nature. Butan-2-ol is the most stable of the isomers due to its hydroxyl being attached to a secondary carbon, giving very favorable steric conditions. 2-Methylpropan-1-ol falls in the middle in terms of stability, while the straight-chain butan-1-ol has the highest energy state and therefore the most exothermic combustion. The fact that such differences are completely unavailable to prediction by the bond enthalpy model, which has the same value of -2489 kJ mol^{-1} for the three isomers, underlines its fundamental limitation. The model takes into account only the quantities and types of bonds, without any regard for the very important role of molecular geometry on energy content. This study hereby illustrates that spatial arrangement of atoms, through its impact on molecular stability and enthalpy of atomization, is a critical determinant of chemical energy in organic compounds.

VI. Conclusion

The following study examined the relationship of molecular structure to the standard enthalpy of combustion of alcohols, focusing on the impact of carbon chain length and branching on $\Delta H^c\ominus$. Two complementary sources were used for data in this research: the standardized values provided in the IB Chemistry Data Booklet for the homologous series analysis and the high-precision experimental measurements included in the NIST Chemistry WebBook for the isomeric comparison. The initial hypothesis-that both structural factors

would provide very significant influences on the combustion energy-was strongly supported. Results indicated that while chain length and branching both play important roles, they function through quite different physical principles. The main results of this study were:

The Additive Effect of Chain Length: Analysis of IB Data Booklet values demonstrated a very good, linear relationship between the number of carbon atoms and the exothermicity of combustion. Increasing the homologous series by one -CH_2- unit added, with each step, approximately -650 kJ mol^{-1} to the $\Delta H^{c}\ominus$. This additive property was successfully modeled using bond enthalpies from the same IB booklet, which predicted the linear trend with very good accuracy. However, this model systematically underestimated the experimental values by 7.0-10.5%, illustrating a key limitation in its application to liquid-phase reactions.

Stabilization by Branching: For structural isomers, NIST data were found to reflect a clear order of stability with remarkable precision. Accordingly, the straight-chain isomer (butan-1-ol) has the most exothermic combustion (-2676.2 kJ mol^{-1}), whereas branched isomers (2-methylpropan-1-ol: -2669.1 kJ mol^{-1}; butan-2-ol: -2660.6 kJ mol^{-1}) have progressively less exothermic reactions. The excellent agreement between two independent NIST studies (Chao and Rossini, 1965; Skinner and Snelson, 1960) with differences below 2.5 kJ mol^{-1} testifies to the reliability of these experimental trends. This trend now directly illustrates that branched alkanes are more thermodynamically stable since they have lower internal energy as a result of less steric strain. The bond enthalpy model failed to reproduce these differences, since all isomers have the same value, once again illustrating its fundamental inability to account for energy differences related to molecular geometry.

This systematic error in the theoretical calculations for the homologous series logically follows from the assumption of gaseous states in the model, which neglects the enthalpy changes related to the vaporization and condensation that accompany the experimental measurements. The use of the IB and NIST data sources complemented each other in this analysis, as IB values established the fundamental trend, while NIST data allowed for precise quantification of the stereochemical effects.

While there were some limitations to this study, particularly in the inherent limitations imposed by the bond enthalpy model and the use of average values, the key findings remain sound. The clear and consistent trends from both data sources are resistant to these limitations and are very well-supported by established principles of organic chemistry and thermodynamics. The results of this study contribute significantly to the molecular determinants of chemical energy content by systematically bridging standardized educational data with primary research databases. This work could be productively extended by exploring other homologous series using NIST precision data, investigating more complex branching patterns, or employing computational chemistry to quantify steric strain. This study confirms that molecular structure is a definitive predictor of fuel energy, with implications in energy science and technology for compound design and selection, while it also illustrates the benefit of combining curriculum-based resources with professional scientific databases for comprehensive chemical analysis.

Bibliography

[1]. Atkins, Peter, and Julio de Paula. Physical Chemistry. 9th ed., Oxford University Press, 2010.
[2]. Brown, Theodore L., et al. Chemistry: The Central Science. 14th ed., Pearson, 2018.
[3]. Chao, J., and Frederick D. Rossini. "Heats of Combustion, Formation, and Isomerization of Nineteen Alkanols." Journal of Chemical & Engineering Data, vol. 10, no. 1, 1965, pp. 37-33.
[4]. International Baccalaureate Organization. Chemistry Data Booklet. 2015.
[5]. Clark, Jim. "Bond Enthalpies." Chemguide, 2019.
[6]. McMurry, John. Organic Chemistry. 8th ed., Cengage Learning, 2015.
[7]. National Institute of Standards and Technology. NIST Chemistry WebBook. NIST Standard Reference Database Number 69, 2023, webbook.nist.gov/chemistry/.
[8]. Skinner, H. A., and A. Snelson. "The Heats of Combustion of Some Aliphatic Alcohols." Transactions of the Faraday Society, vol. 56, 1960, pp. 1776-1783.