Comparing the Enthalpy Changes of Combustion of Different Alcohols

I am going to perform an investigation with the aim of finding the enthalpy change of combustion (ΔH_c) of several different alcohols. I will then compare these results and attempt to show how and why the ΔH_c of an alcohol varies according to its molecular structure.

Planning

Equipment apparatus and materials:
- Copper calorimeter
- Metal draught excluder
- Thermometer
- Digital scales (capable of mass readings given to at least 2 d.p.)
- Clamp stand
- Spirit burners containing the alcohols which will be investigated:
  - Methanol (CH_3OH)
  - Ethanol (C_2H_5OH)
  - Propan-1-ol (C_3H_7OH)
  - Propan-2-ol (C_3H_7OH)
  - Butan-1-ol (C_4H_9OH)

Method

Set up apparatus as shown in the diagram
Pour 200 cm³ water into the copper calorimeter
Take initial temperature reading of water
Weigh the spirit burner with the lid on
Light spirit burner
Stir water often and extinguish the spirit burner once the water temperature has risen by around 20°C
Take final temperature of water
Weigh the spirit burner with lid

Diagram

The metal draught excluder will prevent any breeze or rush of air that may occur from carrying away any of the heat energy produced by the burning of the alcohol. It will also help to prevent heat being lost by radiation, and will help channel the heat of a large flame onto the base of the calorimeter.

The length of the wick must be kept as similar in length as possible throughout to avoid some alcohols burning at different rates to others, and therefore having different amounts of heat lost. The flame must be kept fairly small, so as to avoid excess heat passing the calorimeter in large quantities and escaping. To ensure this, I shall attempt to keep each wick protruding 0.5cm from the spirit burner.

The same calorimeter must be used throughout to avoid any differences in heat conductivity that might otherwise occur. It must be left to cool for several minutes after each run and any soot that builds up will be cleaned off so that it cannot hinder the thermal conductivity of the calorimeter.

The spirit burner must be weighed with the lid on to avoid alcohol evaporating whilst the weighing is taking place. This would result in an inaccurate record of the weight difference in each run. For the same reason, the lid must be kept on at all times when the spirit burner is not lit.

The water must be stirred regularly throughout the investigation so that the temperature of the water remains constant throughout and the reading given by the thermometer accurately reflects the heat absorbed by the water.

I will attempt to keep the temperature rise of each run similar so that results can easily be compared roughly without the need for calculations. This is also important because the amount of energy absorbed by water for an increase in temperature does not remain exactly constant – it is a curve – water needs to absorb more energy to change state, so a given amount of energy will not cause 200cm³ of water at 20°C to raise in temperature by exactly the same amount as 200cm³ of water at 70°C. Whilst this will probably not effect my investigation much (as the final temperatures will always be in a relatively small range), it may be worth considering.

Risk Assessment

Do not inhale alcohol fumes
Take care not to touch the calorimeter or draught excluder immediately after the experiment, as they will be hot.
Take care not to spill alcohol on anything, as it could ignite.
Do not stand with your face directly above the calorimeter if the flame is strong as the hot air could burn you.
Keep wick length relatively low or the flame will be very high.

Theory

It is known that 4.2J of energy are required to increase the temperature of 1g of water by 1°C. Using this known value, I can calculate how much energy has been absorbed by the water, and therefore the enthalpy change of combustion of one mole of the alcohol.

Results

Alcohol	Weight Before (g)	Weight After (g)	Weight Diff. (g)	Temp Before (°C)	Temp After (°C)	Temperature Diff. (°C)
Methanol (1)	241.16	239.82	1.34	23.0	41.5	18.5
Methanol (2)	238.59	237.17	1.42	21.5	42.0	20.5
Ethanol (1)	227.66	226.37	1.29	22.5	41.0	18.5
Ethanol (2)	226.37	225.03	1.34	23.0	42.0	19.0
Propan-1-ol (1)	255.87	254.78	1.09	21.5	41.0	19.5
Propan-1-ol (2)	251.40	250.30	1.10	21.0	42.0	21.0
Propan-2-ol (1)	235.32	234.17	1.15	23.0	44.0	21.0
Propan-2-ol (2)	230.38	228.61	1.77	20.5	40.5	20.0
Butan-1-ol (1)	242.52	241.68	0.84	21.0	41.0	20.0
Butan-1-ol (2)	228.31	227.23	1.08	21.0	42.0	21.0

Calculations

Here is an example of how I will obtain ΔH_c for each of the alcohols. This calculation is for the first trial of methanol.

1. It takes 4.2J to heat 1g water by 1°C. Therefore the amount of energy taken in by the water is

200 x 18.5 x 4.2 = 15540J

2. How many moles are there in the methanol that was used up? 1.34g methanol =

1.34/32 = 0.041875 moles

3. If 0.041875 moles methanol released 15.54kJ then 1 mole will release

15.54/0.041875 = 371kJ (3sf)

So ΔH_c of methanol is –371kJ.

Using this calculation, I have worked out the other ΔH_c values.
The following table shows my calculated results.

Alcohol	Enthalpy Change of Combustion	Average Enthalpy Change of Combustion
Methanol (1)	-371 kJ	-380 kJ
Methanol (2)	-388 kJ	
Ethanol (1)	-554 kJ	-551 kJ
Ethanol (2)	-548 kJ	
Propan-1-ol (1)	-902 kJ	-932 kJ
Propan-1-ol (2)	-962 kJ	
Propan-2-ol (1)	-920 kJ	Not relevant (-920 kJ)
Propan-2-ol (2)	-569 kJ	
Butan-1-ol (1)	-1480 kJ	-1345 kJ
Butan-1-ol (2)	-1209 kJ	

NB. Calculated values are given to the nearest whole number.

The ΔH_c value for the second trial of propan-2-ol is shaded red because it is clearly anomalous – not only does it not agree with the result obtained for the first trial, but it is also out of place with the general trend of the rest of the results. This means that the average of the two results is irrelevant. This causes a problem in that I will have to use the value obtained from the first trial, which could also be inaccurate.
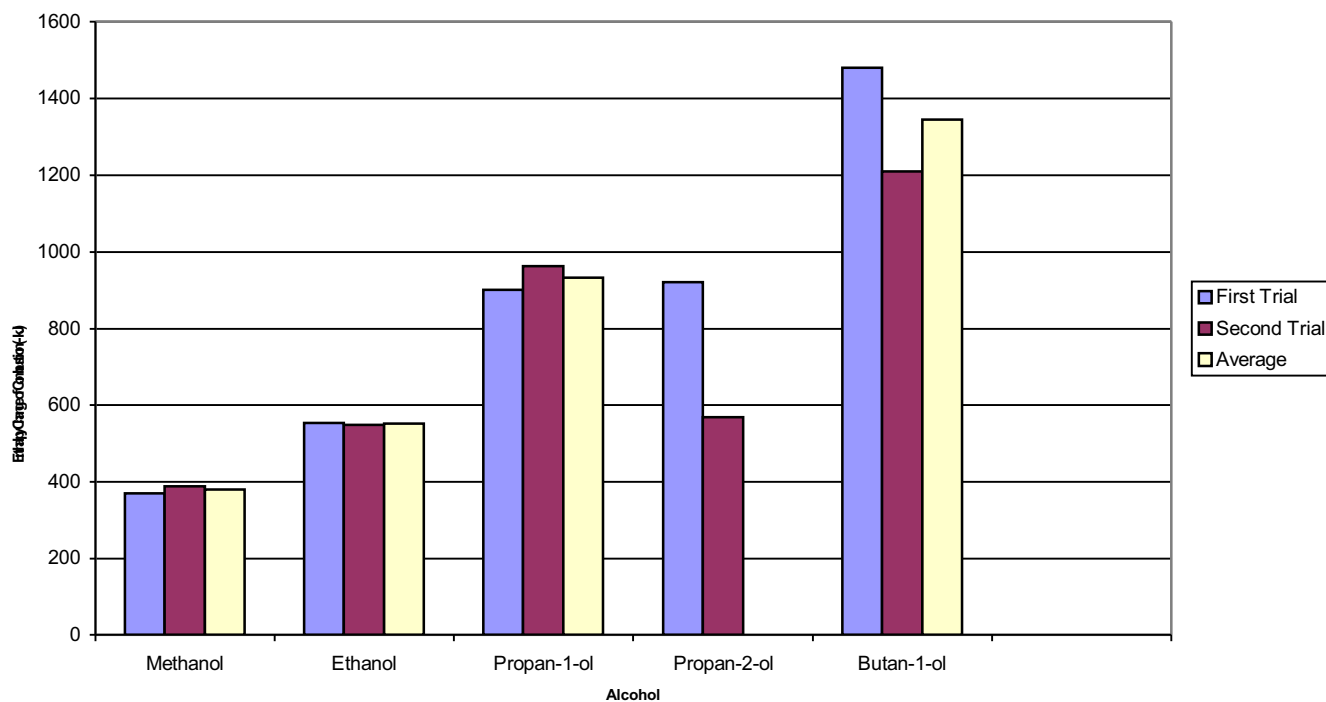
I have also drawn a graph with 'no. of carbon atoms' along the x-axis. I have omitted propan-2-ol in this graph.

The line of best fit drawn is not definitely accurate – there is not enough data to state that it is. It only identifies a general trend. In fact, a curve may actually be more appropiate.

The product moment correlation coefficient is a useful value that shows how strong the linear correlation is between two sets of data. The formula for calculating the value of the product moment correlation, 'r' is:

$$r = \frac{\sum xy - \frac{\sum x \sum y}{n}}{\sqrt{\left[\left(\sum x^2 - \frac{\sum x^2}{n}\right)\left(\sum y^2 - \frac{\sum y^2}{n}\right)\right]}}$$

This means that r = 0.969 (3 sf), which indicates a strong positive linear correlation, as r can only be as large as 1 for absolute correlation. However, this does not include any data gathered for propan-2-ol. Also, it must be noted that the actual enthalpy changes are becoming more negative rather than more positive, although this wouldn't affect the strength of the correlation.

Analysis

The evidence I have gathered shows a clear trend – in general, the enthalpy change of combustion becomes more negative as the alcohol molecules become larger.

This can be explained by showing the two stages involved when the combustion of an alcohol takes place. Firstly, the existing bonds that make up the alcohol and oxygen are broken, and this requires energy (this energy that we provide is called activation energy). Secondly, new bonds are made for the products of the reaction – in the case of combustion these are water and carbon dioxide. The process by which bonds are made gives out energy. It is the overall sum of all of the energy taken in (giving a positive ΔH_c) and the energy released (negative ΔH_c) that decides the overall enthalpy change of combustion for the reaction.

As you go up through the alcohols, you are simply adding one C atom and 2 H atoms each time to the formula of the alcohol. As each bond that makes up both the products (the alcohol and oxygen) and the products (carbon dioxide and water) has a roughly set enthalpy value, the relationship between the ΔH_c of the alcohols could be expected to be a linear relationship.

However this relationship doesn't take into account the existence of isomers of these alcohols. The results obtained from my investigation referring to the only non-straight-chain isomer, propan-2-ol, are not very reliable. I only have one value that is vaguely accurate, but I cannot base much upon this one result. The result that I do have seems to be very close to the value for propan-1-ol. It is slightly more positive than one of the trials and slightly more negative than the other. Any difference between the two isomers of propanol can be put down to isomerism.

I would actually expect the ΔH_c of propan-2-ol to be less negative that that for propan-1-ol for this reason: As the alcohol molecule does not form such a straight chain in propan-2-ol as it does in propan-1-ol, the molecules cannot sit so close to one another. This is mainly due to the position of the OH side group in the molecule altering the position of the electromagnetic poles.

From the results, I could form an equation to roughly predict the enthalpy change of combustion of any straight-chain alcohol. However I cannot assume that the obtained results are actually accurate. The enthalpy changes of combustion of these alcohols has been accurately calculated and this table shows the actual values compared with the calculated values.

Alcohol	Average obtained ΔH$_c$	Actual ΔH$_c$	Error
Methanol	-380 kJ	-726.0 kJ	346 kJ
Ethanol	-551 kJ	-1367.3 kJ	816.3 kJ
Propan-1-ol	-932 kJ	-2021.0 kJ	1089 kJ
Propan-2-ol	-920 kJ	-2005.8 kJ	1085.8 kJ
Butan-1-ol	-1345 kJ	-3328.7 kJ	1983.7 kJ

This table illustrates that the evidence gathered is not accurate, but it does still show a similar general trend. It also shows several other things.

As predicted, the ΔH$_c$ of propan-2-ol is indeed less negative than that of propan-1-ol.

As the calorific values of the alcohols being investigated increased, so the error between the value obtained and the actual value increased. This is probably because more heat was being lost into the atmosphere from the combustion, as more energy was being released per unit of time than with the alcohols of lower calorific value. This means that the actual linear relationship will be different, but since for the actual values, $r = 1.00$ (3sf) there is still a very strong linear correlation (almost a perfect correlation in fact).

Evaluation

Two main problems appear from the evidence gathered. Firstly, one of the trials for the alcohol propan-2-ol was anomalous, meaning that I had to rely on just one reading.
Secondly, all of the results obtained from the evidence gathered are quite different to the actual values, as the above table shows.

One explanation for the anomalous result obtained with the combustion of propan-2-ol is that the wick on the spirit burner was too high. If this was the case, the flame would have been higher than on the other trials, and as a result more heat would have been lost into the atmosphere, rather than being absorbed into the water. In general, the height of the wick was very difficult to keep constant throughout, especially as the wick was never flat on the surface, and could therefore not be measured.
Perhaps one way that this could be solved were the experiment to be repeated is to actually cut the used section of the wick off of the end so that the length and capacity for holding alcohol could be kept constant.

Another problem was that much of the heat was escaping around the sides of the metal draught excluder, and therefore the calculated figure for the enthalpy change of combustion was less negative than the actual figure.
One solution to this would be to use a calorimeter with a larger base surface area, so more energy could be absorbed by the water. Also, the draught excluder could be narrower so that it prevents more heat from escaping.

Although not a significant source of error in this investigation, the use of a standard thermometer would prevent a very accurate result in an investigation which had neither of the above two problems. It would therefore be useful to use a more accurate digital thermometer which could record peak temperature, so that there would be no problem caused by a delay in actually taking the reading.

The results I obtained are sufficient to show the general trend in the change of the enthalpy changes of combustion of the alcohols as the molecules get larger, i.e. the changes become more negative as the alcohol grows in length.

However, the results are not sufficiently accurate to draw up any formula to predict the enthalpy change of combustion for any alcohol molecule.

Also, not enough alcohols were available to draw up any proper conclusions about how isomerism affects the enthalpy change of combustion.

It would be interesting to extend this investigation with more alcohols, for instance alcohols up to octanol. It would also be interesting to extend this investigation so that it incorporates more isomers of the alcohols, for instance three isomers of pentanol could be used:

$CH_3(CH_2)_3CH_2OH$ — Pentan-1-ol

$CH_3CH_2CH_2CH(OH)CH_3$ — Pentan-2-ol

$CH_3CH_2CH(OH)CH_2CH_3$ — Pentan-3-ol