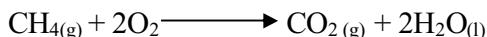


The enthalpy change of combustion of alcohols

Aim

The aim of this experiment is to investigate the enthalpy change of combustion for a variety of alcohols and determine how the number of carbon atoms affects the combustion of the alcohol.

'The **standard enthalpy change of combustion** is the enthalpy change when one mole of an element or compound reacts completely with oxygen under standard conditions. For example a pressure of 100 kilopascals, a temperature of 298 Kelvin, solutions must have a concentration of 1.0 mol/dm³ and also the reactants and products must be in the physical states e.g. solid, liquid or gas, that are normal for these conditions.'¹ An example of a combustion reaction of methane is show below.



Prediction & Development of problem

I predict that the enthalpy change of combustion will increase as the number of carbon atoms within the alcohol increases. Alcohols form a homologous series. A homologous series is formed by molecules with different carbon chain lengths but with the same functional group and all have similar chemical properties. These aliphatic alcohols have the general formula C_nH_{2n+1}OH, (where n is the number of carbon atoms present in the molecule.) The alcohols are given names of the alkane with the corresponding number of carbon atoms with the final 'e' being replaced with 'ol'. Alcohols all have similar properties, for example ethanol and methanol is freely miscible in water. 'Miscibility is the measure of how easily a liquid mixes.'² When water and ethanol mix, some of the hydrogen bonds between the molecules in the separate liquids are broken, hydrogen bonds then form between the water and the ethanol. The miscibility of alcohols in water decreases with increasing hydrocarbon chains. Alcohols can also be used as fuels as they have high enthalpies of combustion. However there are other chemicals, which are better fuels and are cheaper and are therefore more widely used. Unleaded petrol contains about 5% methanol the advantages of methanol are that it burns cleanly however it is more toxic than ethanol and produces less energy per litre than petrol. Ethanol is used as a fuel in the form of methylated spirit. This spirit burns with a light blue flame. Due to its volatility, which is explained below, the flame can be hard to detect in sunlight, so when filling stoves accidents can occur. However alcohols are relatively light therefore campers can prefer carrying these to other chemicals. In some areas methanol is used for racing cars and ethanol is blended with petrol to make cheaper motor fuel. More useful fuels can generally be made from chemicals with large hydrocarbon chains; therefore the fractional distillation of crude oil is more widely used to produce fuels. Alcohols are more widely used as solvents as they contain a polar hydroxyl group. They also mix with many other compounds, and will dissolve in some ionic compounds. More importantly in this investigation is the volatility of alcohols. 'Volatility is the ease with which a liquid turns into a vapour'³. The attractive forces between the C-H atoms etc are known as covalent bonds. These intramolecular forces are relatively strong in alcohols

Covalent bond



There are also intermolecular attractions between the alcohol molecules known as hydrogen bonds. Hydrogen bonds are caused by permanent dipole to dipole attractions within the molecules. Dipoles are caused by the difference in electronegativity between two atoms. Electronegativity is the ability of an atom to attract the bonding electrons from within a covalent bond towards itself. Oxygen is more electronegative than hydrogen and carbon and therefore attracts the electrons towards itself creating a partially negative charge on the oxygen atom this in turn means that the hydrogen atom and carbon atom become partially positively charged.

The movement of electrons due to the electronegativity of one or more atoms creates a partial charge or δ^- . This is known as a dipole. The molecule as a whole is said to be polarised. As the dipoles are permanent it can be said that the molecule is permanently polarised.

Due to the polarisation of the molecules, alcohols have generally higher boiling and melting points than you might predict points and hence a low volatility and are liquid at room temperature.

When reacted with oxygen, which has a much greater electronegativity than hydrogen, the remaining hydrogen atoms (which are not bonded to the oxygen atom,) readily form new stronger bonds with the oxygen atoms forming H_2O . The carbon atoms also form bonds with the oxygen atoms forming carbon dioxide.

The combustion of alcohols is an exothermic reaction. The law of conservation of energy states that energy can neither be created or destroyed it is only transferred from one form to another. For a reaction to take place bonds must be broken and new bonds formed. When bonds are broken energy is absorbed, this is an endothermic process. When bonds are formed energy is released usually in the form of heat and light, this is known as an exothermic reaction. As in the combustion of alcohols, if the energy released when bonds are formed is greater than the energy absorbed in breaking the bonds the overall reaction is exothermic. The bonds, which are broken in this reaction between an alcohol and oxygen, are C-C, C-H, O=O and C-O. The bonds made are C=O and H-O. However the bond energies between the bonds which are formed are greater than the bond energies of the bonds which are broken.

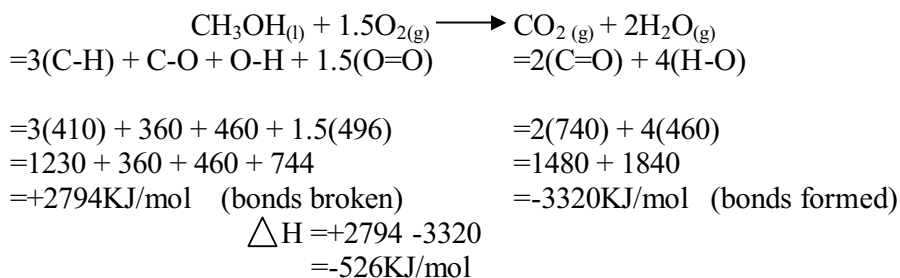
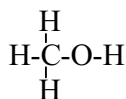
Particularly the C=O bond which is almost twice as large as the bond energy within the C-C bond. The significance of this is that as the carbon chains increase in length more C-C bonds are broken, however more C=O bonds are formed. As the carbon

chain length increases the difference between the bond energies of bonds broken and bonds formed increases in favour of the exothermic reaction (bonds formed). I calculated the predicted value of the enthalpy change of combustion using bond energy calculations to support my prediction. I have also decided to investigate whether the enthalpy of combustion is effected by whether the alcohol is a straight chain or a branched alcohol. I have therefore also calculated the overall bond energy for the isomer of butanol, butan-2-ol.

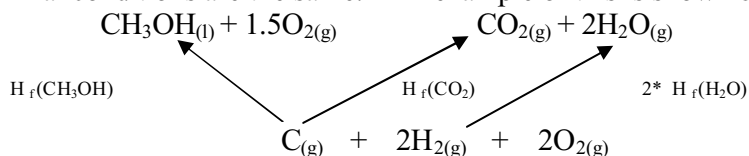
Theoretical bond enthalpy calulations

BOND (KJ/mol)	
H-H	+436
C-C	+350
C=C	+610
C-H	+410
O=O	+496
O-H	+460
C-O	+360
C=O	+740

Methanol CH₃OH

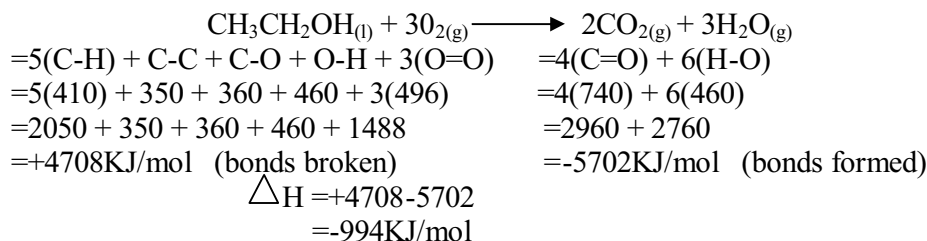
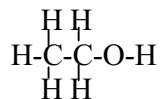


A Hess cycle could also be used to calculate the enthalpy change in combustion. Hess's Law states that 'The total enthalpy change for a chemical reaction is independent of the route by which the reaction takes place, providing the initial and final conditions are the same.'⁴ An example of this is shown below;

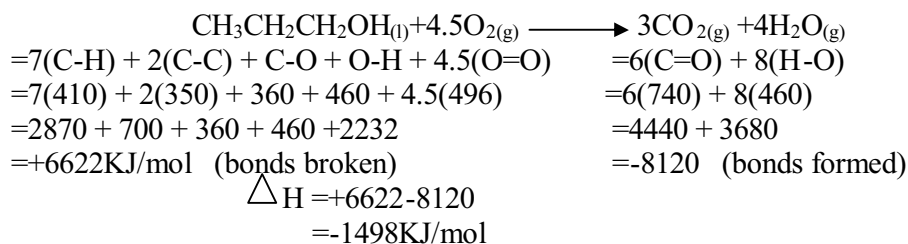
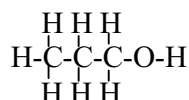


$$\text{H}_c(\text{methanol}) = - \text{H}_f(\text{CH}_3\text{OH}) + \text{H}_f(\text{CO}_2) + 2 \text{H}_f(\text{H}_2\text{O})$$

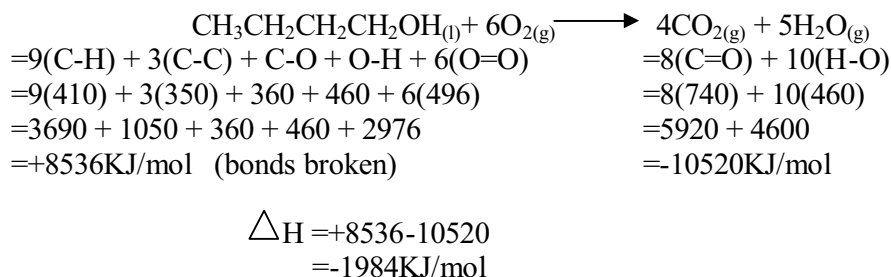
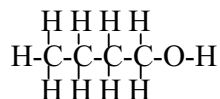
Ethanol $\text{CH}_3\text{CH}_2\text{OH}$



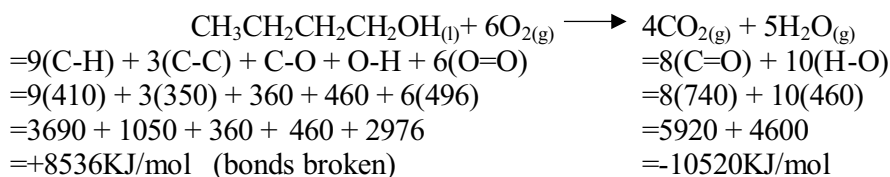
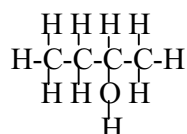
Propanol $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$



Butanol $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$



Butan-2-ol $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$



$$\begin{array}{l} \Delta H = +8536 - 10520 \\ = -1984\text{KJ/mol} \end{array}$$

Due to Butan-1-ol and Butan-2-ol having the same molecular structure the estimated enthalpy change of combustion is therefore the same as the same bonds are being broken as they are formed in both alcohols. I therefore predict that positioning of the OH has no effect on the enthalpy of combustion.

It can be seen from the structures of these alcohols that the chain length increases by CH_2 each time. I therefore predict that the increase in enthalpy of combustion will be proportional to the length in carbon chains, as the number of bonds increases constantly as the chain length increases. I therefore have made an informed prediction that a graph with the following trend will be seen.

Safety

Refer to Risk assessment in the appendix.

Trial Run

In order to measure the enthalpy change of combustion I had to burn the alcohol and record the increase in temperature in a set volume of water, and record the change in mass of the alcohols. I can then use the equation $\Delta H = mc\Delta t$, (where m is the mass of water, c is the heat capacity of water which is known as 4.18, and t is the temperature.) I decided to test methanol in my trial run to see if my experiment worked correctly and to familiarise myself with the equipment.

Apparatus

Crucible
Rockall wool
Thermometer
Copper calorimeter
clamp stand
clamp
Methanol
Water
Measuring cylinder

- First set up apparatus as shown in the diagram above.
- Measure 100cm^3 of water using a measuring cylinder and place in the copper calorimeter
- Record the starting temperature of the water (All temperatures are recorded to the nearest degree.)
- Place 1cm^3 of methanol on the rocksil wool in the crucible.
- Record the mass of the crucible containing the wool and alcohol. (All masses are measured on the balance in grams to 2.d.p.)
- Light the alcohol.
- Leave until the alcohol has completely combusted and the flame is extinguished
- Record the final temperature of the water using the thermometer.
- Record the change in mass of the crucible and rocksil wool.
- Calculate the change in mass by subtracting the starting mass by the final mass
- Also calculate the change in temperature by subtracting the final temperature from the original temperature.
- Calculate the enthalpy change of combustion the recorded results.

After performing my trial run I realised there were several faults in the system. The change in temperature I recorded was 5 degrees however when compared to my fellow peers who were also investigating the enthalpy change of combustion of alcohols I discovered that there recorded results of the change in temperature for the same volume of methanol were 18 degrees, 9 degrees and 6 degrees. I therefore decided that the results that would be recorded using this method and this set of apparatus were to crude. Too much heat was being lost into the surroundings; also the copper calorimeter would have conducted heat away from the water reducing the increase in temperature. I also felt the volume of water was to great for the amount of methanol being combusted and therefore a lot of energy would have been required to increases the temperature of the water dramatically. There was also no stirring device to make sure that the heat was equally spread throughout the water easily. The alcohol also spread out which increased its surface area, which may have also had an effect on the results. I have therefore decided to modify this method before repeating any results, as they would be too inaccurate.

Apparatus

5 spirit burners
copper calorimeter lagged with rocksil wool

50cm³ of water
Alcohols (methanol, ethanol, propanol,
Butan-1-ol and Butan-2-ol)
Thermometer (to the nearest degree)
Plastic stirrer
Draught excluders
50cm³ pipette
Plastic lid
(this contained two holes
for the thermometer and the stirrer)
Clamp stand
Clamp
Stop clock
Balance
Matches

Method

- Place alcohols in spirit burners and label clearly
- lag side surfaces of the calorimeter with rocksil wool to prevent some of the heat loss and also use a plastic lid.
- Measure out 50cm³ of water using a bulb pipette as this is much more accurate than a measuring cylinder. Weigh the mass of the calorimeter then place the water into it and record the final mass, the difference between the two values should check that there actually is 50(g) or 50cm³ of water being used.
- Make a non-conducting stirrer using a plastic drinking straw, which bends at one end.
- Set apparatus as show above.
- Weigh the spirit burner containing one of the alcohols on the balance (grams to 2.d.p)
- Record the starting temperature of the water in the calorimeter at time is zero, (with a thermometer to the nearest degree)
- Make sure the bottom of the calorimeter is 12cm from the base of the clamp stand, (this ensures that the experiment is a fair test)
- Light the spirit burner with a match and measure the height and width of the flame.
- Extinguish the flame and adjust the size of the wick so that the size of the flame is 1cm in height and width. This may need to be checked and adjusted again until it is correct.(This is to ensure the surface area of the flame remains the same, which will also maintain a fair test.)
- Light the spirit burner and simultaneously start the stop clock.
- Record the increase in temperature every 30 seconds. (This is not necessary in order to determine the enthalpy of combustion, However time allowing I thought it might be interesting to compare the rates of reactions of the different alcohols.)
- Continue to stir the water and allow the alcohol to burn for five minutes
- Extinguish the flame and record the final temperature.
- Weigh the spirit burner containing the remaining alcohol on the balance.

- Calculate the enthalpy change of combustion using the formula $\Delta H = mc\Delta t$ (where m is the change in mass, c is the heat capacity of water which is known as 4.18 and t is the change in temperature.)
- Repeat experiment twice more for each alcohol and calculate the enthalpy of combustion for each and then take an average.
- Repeat the process with the other alcohols, the results of four alcohols are required to plot a graph each of which must have been repeated three times

Trial Run

I performed a trial run using this modified method to familiarise myself with the new apparatus and the procedure. The change in temperature using this method was much greater and easier to measure. It was also a lot more accurate as less heat was lost into the surroundings and from the copper calorimeter. I therefore decided to carry out this experiment fully using this method using at least four alcohols and repeating each three times so that an average enthalpy change of combustion can be recorded which should be more accurate.

My first reading of methanol was very similar to that gained during my trial run. I therefore decided to include my trial run as one of the repeat readings of methanol as time for this experiment was limited.

Fair Test

In order for this experiment to be a fair test certain variables must be taken into consideration.

The dependant variable in this experiment is the change in temperature and the change in mass, which both contribute to the difference in enthalpy of combustion between the different alcohols which is also a dependant variable as this is what is eventually being measured.

The independent variables in this experiment are the different alcohols, which vary in their lengths of carbon chains.

The controlled variables which must be kept constant are the height of the calorimeter from the bottom of the clamp stand which I set as 12cm. Also the arrangement of the draught excluders and their distance from the apparatus must remain the same. Also the size of the wicks of the spirit burners must be kept constant so the size and therefore surface area of the flame is the same for each alcohol I cut the wick so that when lit the size of the flame was 1cm in height and width.

I then calculated the enthalpy of combustion for the readings and took the average of each alcohol. I then compared them to the values of enthalpy of combustion stated in a data book. The same trend was seen however my values differed quite a lot from that of the ones in the book. This could have been due to the following reasons; Heat was still being lost into the surrounding and was not being recorded. Also although the calorimeter was lagged and it now had a plastic lid heat was also still being lost through holes in the lid which were made in order to allow for the thermometer and the plastic stirrer. As people walked past draughts were causing the flame to flicker and it was not always the size it should have been and did not always point in the correct direction. I also noticed that a black substance was building up on the under side of the calorimeter. This substance was soot this meant that the carbon was not fully combusting to form carbon dioxide as it should, which meant that the alcohol was not fully combusted and therefore the results for the combustion of the alcohol

are likely to be wrong. I therefore decided that there must still be faults in the system and I decided to modify my method once again. There was also quite a high percentage of error created by the apparatus used. For example the mass of the alcohols was measured on a balance recorded to two decimal places. The mass is therefore recorded to the nearest 0.01 (g). The %error can be calculated as follows,

$$\frac{0.01}{\text{mass (g)}} \times 100 = \% \text{error}$$

The temperature was measured on a thermometer to the nearest degree therefore the % error will be,

$$\frac{1}{\text{temperature (}^{\circ}\text{C)}} \times 100 = \% \text{error}$$

The bulb pipette that measures the volume of water will also cause a % of the errors caused. The pipette that was used in this investigation was quoted as 0.25%

It can be seen without the need to actually calculate these values that the % of errors are going to have quite an effect of the accuracy of the results. The %error for the temperatures is relatively large for the error caused by an instrument particularly when considering that the error occurs on the original temperature and the final temperature, and the difference between the temperatures means that the % error could double. Therefore in my modified method I will use a thermometer that measures to the nearest half a degree, and I will record the mass of the alcohols to three decimal places to improve the accuracy of my next set of results.

Apparatus : The flame calorimeter

Thermometer
 clamp stand
 clamp
 spirit burners
 stirrer
 Copper spiral
 Suction pump
 rubber tubing
 Water 550cm³
 Alcohols
 matches
 Balance
 Glass calorimeter

Method (after two modifications)

- Place the alcohols in small clearly labelled spirit burners.

- Place 550cm³ of water into the apparatus, containing the copper spiral, and the metal stirrer. (A metal stirrer had to be used as this was attached to the apparatus.)
- Clamp the calorimeter, and also its base onto the clamp stand
- weigh the spirit burner containing the alcohol and its lid on the balance which can be recorded to 3.d.p
- Record the starting temperature of the water using a thermometer to 0.5 of a degree as this will make the results a lot more accurate.
- Lower the base of the calorimeter and place the calorimeter in its designated position.
- Start the suction pump, which is connected using the rubber tubing to draw air through the apparatus so that the combustion reaction can occur with limited heat loss.
- Light the spirit burner and replace the base of the calorimeter.
- Wait for the temperature to rise several degrees while continuously stirring the water.
- Extinguish the flame and switch off the suction pump.
- Keep stirring for a further minute to ensure that the temperature of the water increases to its true value.
- Record the final temperature.
- Weigh the spirit burner containing the remaining alcohol and its lid.
- Calculate the change in temperature and change in mass
- Use these results calculate the enthalpy change of combustion
- Repeat the above process using the other alcohols.
- Ideally the alcohols should all be repeated three times and an overall average taken. However time is limiting so I will repeat each alcohol once and compare the accuracy of these results with the results of my previous methods, my bond energy calculations and the values obtained from the data book.

Results

I can calculate the enthalpy change of combustion of the alcohols using the equation $\Delta H = mc\Delta t$ (where m is the mass of water, c is the heat capacity of the water which is known as 4.18 and t is the increase in temperature.)

Below are the results I recorded for the three readings of methanol when using the copper calorimeter.

Methanol

$$\Delta H = mc\Delta t$$

$$= 50 \times 4.18 \times 53$$

$$= 11077\text{J}$$

$$= 11.077\text{KJ}$$

$$\text{moles} = \text{change in mass} / \text{MR}$$

$$= 1.38 / 32$$

$$= 0.043\dots$$

$$\Delta H_c = 11.077 / 0.043\dots$$

$$= -256.86\text{KJ/mol (1}^{\text{st}} \text{ reading)}$$

$$\Delta H = 50 \times 4.18 \times 51$$

$$= 10659\text{J}$$

$$\begin{aligned}
 &= 10.659 \text{ KJ/mol} \\
 \text{moles} &= 1.51/32 \\
 &= 0.047.. \\
 \Delta H_c &= 10.659/0.047... \\
 &= -225.89 \text{ KJ/mol (2}^{\text{nd}} \text{ reading)}
 \end{aligned}$$

$$\begin{aligned}
 \Delta H &= 50 \times 4.18 \times 50 \\
 &= 10450 \text{ J} \\
 &= 10.45 \text{ KJ} \\
 \text{moles} &= 1.51/32 \\
 &= 0.047.. \\
 \Delta H_c &= 10.45/0.047... \\
 &= -221.46 \text{ KJ/mol (3}^{\text{rd}} \text{ reading)}
 \end{aligned}$$

$$\begin{aligned}
 \text{Average } \Delta H_c &= (-256.86..-225.89..-221.45..)/3 \\
 &= \underline{-234.73 \text{ KJ/mol}}
 \end{aligned}$$

The rest of my results using the copper calorimeter and the flame calorimeter have been recorded in tables using formulas to calculate the results in the same way in Microsoft excel.

Analysis

I plotted my results from both the methods using the copper calorimeter and the flame calorimeter on graph showing enthalpy change of combustion against the carbon chain length.

From looking at graph two (using the flame calorimeter) a clear trend can be seen in which as the number of carbon atoms in the chain increases the enthalpy change of combustion becomes increasingly negative as the reaction becomes more exothermic. This trend is not shown, as clearly in graph one, this is because these results are a lot less accurate.

I calculated the gradient of graph two, which I am assuming, is the enthalpy change of combustion per carbon atom.

$$\begin{aligned}
 \text{Gradient} &= -1767/4 \\
 &= -441.75 \text{ KJ/mol.}
 \end{aligned}$$

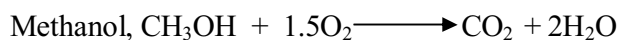
The enthalpy change of combustion increases by -441.75 per carbon atom in the chain length. I can therefore calculate the approximate value for the enthalpy change of combustion of pentanol, that I would have been likely to record had there been enough time to perform this remaining alcohol. I can do this in two ways by either adding -441.75 to the result that was recorded for the previous alcohol(butan-1-ol). The value for butan-1-ol was -1761.139KJ/mol, therefore the estimated value for pentanol would be -1761.139 + -441.75

$$= -2202.75 \text{ KJ/mol}$$

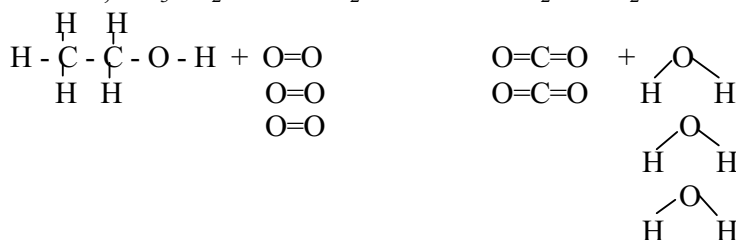
Extrapolating the graph could also produce a similar value. This produces a value of -2240KJ/mol.

The trend in these results can be explained using a variety of scientific knowledge. The main reason for the increases in enthalpy of combustion is determined by the strength of the different types of bonds. Primarily the difference between the bond energies of the C-C atoms and the C=O atoms. The bond energy value between the C-C atoms is 350KJ/mol. When reacted with oxygen as in this combustion reaction

C=O is formed which has a much greater bond energy value of 740KJ/mol. This value is twice that of the C-C bond. From Studying the structure and covalent bonds that are broken and formed in the combustion reaction of the alcohols the relevance of this can be seen.



In this example there are no C-C covalent bonds, However the strongest bond present in the alcohol is the O-H bond, which has a value of 460KJ/mol. If you look at the bonds formed it can be seen that four of these O-H bonds are formed quadrupling the value (460x4)=1840KJ/mol. Also two of the strongest bonds are formed which are C=O bonds these each have a bond energy value of 740KJ/mol. The bonds formed therefore stronger than the bonds broken and hence more heat is released, and the reaction is exothermic.



From this I can see that only one C-C bond is broken however now four C=O bonds are formed. As the carbon chain length increases by one there is an increase in one C-C bond, two C-H bonds and 1.5 O=O bonds. The total bond energy for these bonds is 1914KJ/mol. These are the extra bonds, which are being broken, and are therefore the endothermic increase when the carbon chain length is increased by one. When the chain length is increased by one the extra bonds formed are 2(C=O) and 2(O-H) The bond energy value for these bonds is -2400KJ/mol. This is the increase in the exothermic reaction when the carbon chain length is increased by one. The exothermic reaction is greater than the endothermic reaction and that is why the exothermic reaction increase as the carbon chain length increases the value for this increase can be calculated by adding the two values.

$$+1914 + -2400$$

$$=-486$$

This value is the increase in enthalpy change of combustion for the overall reaction per carbon atom in the chain length. This is a more accurate value then the one I calculated from finding the gradient of my graph. However the difference between the two values does show that my results were quite accurate. I can calculate the error in my results by finding the difference between the two values and displaying this as a percentage of the calculated value.

$$\% \text{Error} = \frac{-486 - -441.75}{-441.75} \times 100$$

$$= \frac{-486}{-44.25} \times 100$$

$$\frac{-486}{5} = 9\%$$

This shows that my results were definitely reliable and generally accurate. However there is one anomalous result on graph two with the alcohol propanol, which has three carbon atoms in its chain length and an enthalpy of combustion of -1130.656KJ/mol. From extrapolating the line of best fit I deduced a value of -1360KJ/mol this is more likely to be the value recorded had I had time to do repeat readings for the alcohols.

A line of best fit is hard to draw on graph one as the results are less accurate and I am unsure which are the anomalous results. I therefore decided to draw the line, which followed the trend set by the actual results from the data book, as this line went through the first three points on the graph.

$$\begin{aligned} \text{The gradient of this graph} &= \frac{-490}{2} \\ &= -245 \text{KJ/mol per carbon atom in the chain} \end{aligned}$$

The error between this value and the calculated value is going to be a lot greater than that calculated from graph one.

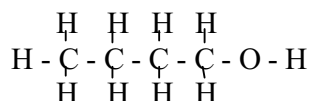
$$\begin{aligned} \% \text{Error} &= \frac{-486 - (-245)}{-486} \times 100 \\ &= \frac{-241}{-486} \times 100 \\ &= 49.6\% \end{aligned}$$

This value is dramatically larger, but this was expected due to error noted in the experiment involving the copper calorimeter.

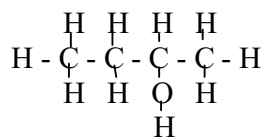
From finding the gradient of the results found in the data book I determined that the most accurate result for the enthalpy change of combustion per carbon atom is -600KJ/mol per carbon atom in the chain length. This shows that even the bond energy calculations are not entirely accurate, as there is a difference of over -100KJ/mol per carbon atom compared to these results. I decided that I would look in other sources to find whether the bond energy values varied from textbook to textbook. There were quite a variety of results published, the C=O bond value varied the most. The lowest value I found was 720KJ/mol and the highest value was 805KJ/mol. That is a difference of 85KJ/mol. This shows how difficult it is to accurately measure the strength of the hydrogen bonds between the molecules.

In my plan I said that I was going to investigate whether the enthalpy change of combustion varied between straight chain molecules and isomers of the molecule by studying the difference between butan-1-ol and butan-2-ol. I predicted that the enthalpy of combustion will remain the same as the molecular structure is the same and therefore the same bonds are being broken and formed. When I calculated the bond enthalpies of both alcohols the result was the same so I felt my prediction was justified. However from looking at the results I recorded on both graphs I no longer agree with my prediction as both of the graphs tell the same story and show that the enthalpy change of combustion for butan-2-ol is lower than that of butan-1-ol. The structure of the alcohols must be the result of this.

Butan-1-ol



Butan-2-ol



The Only difference between these alcohols is that the OH atoms are on different carbon atoms. The OH is on carbon number 1 in butan-1-ol and in on carbon number 2 in butan-2-ol. The enthalpy change of combustion of butan-1-ol is greater than the enthalpy change of combustion of butan-2-ol. This means that in butan-1-ol either less energy is needed to break the bond or more energy is given out in the formations of the new bonds compared to that of butan-2-ol. Both of the alcohols produce the same products which are 4CO_2 and $5\text{H}_2\text{O}$. These products have the same molecular structure and also the same arrangement of atoms. This means that the energy released when the bonds are formed remains the same in both alcohols and therefore the energy required to break the reactant bonds must be the cause of the difference in enthalpy of combustion.

When the alcohols are reacted with oxygen the C-C bonds break up to form CO_2 , eight of the hydrogen atoms react with four external oxygen's to form $4\text{H}_2\text{O}$. The remaining oxygen and two hydrogen atoms, which were part of the alcohol, make up the remaining water molecule, in total producing $5\text{H}_2\text{O}$. It is the ease with which the OH group bonds with one of the neighbouring hydrogen atoms that produces one molecule which results in the difference in the enthalpy change of combustion.

In the straight chain alcohol, butan-1-ol, the bond angle between the OH group and the neighbouring hydrogen atom is small at approximately 109.5 degrees as they are both bonded to the same carbon atom. This means that the hydrogen atom is readily available to react and this reaction requires little external energy to break the hydrogen bond. Butan-2-ol has an OH group on its second carbon atom. This OH group is much further away from another hydrogen atom and it reacts with one bonded to another carbon atom. This means that it does not form a water molecule as easily and requires more energy to break the bonds. Because of this the endothermic reaction using butan-2-ol is greater than that of butan-1-ol. The difference between the endothermic and exothermic reactions in butan-2-ol is less than that of butan-1-ol and the enthalpy change of combustion is therefore less in butan-2-ol than it is in butan-1-ol. The calculated value from graph two for the difference of enthalpy of combustion between thesis alcohols is $-1761.139 - -1166.845$

$$= -594.294 \text{ KJ/mol.}$$

I also decided that I would plot the results I recorded using the copper calorimeter of temperature against time as I thought this would emphasize the increase in the exothermic reaction as the carbon chain length increases. I also calculated the gradients of each of the individual graphs to calculate the increase in temperature per second for each of the alcohols. Butan-1-ol has the largest gradient of 0.39 degrees/second as I would have predicted. This is the most exothermic of the combustion reactions with alcohols and therefore the temperature increases in a shorter period of time.

From this experiment I have therefore determined that the enthalpy change of combustion does increase as the length of the carbon chain increases by approximately -441.75KJ/mol per carbon atom in the chain length. I have also discovered that isomers of an alcohol do have an effect on the enthalpy change of combustion, in which straight chain alcohols have a much greater enthalpy of combustion than the side branched alcohols.

Evaluation

The first method I developed was using a crucible; this was a very crude method and was not accurate at all, so I therefore did not perform this method with any of the alcohols other than ethanol, which was used, for the trial run. There were just too many causes of error using this method, for example there was a substantial amount of heat lost into the surroundings and also through the copper calorimeter which would have conducted the heat away. The alcohol spread out and its surface area increased which may have effected the results, the alcohol was also not contained completely and would have been able to evaporate quite easily. The volume of water used was also too large for the small amount of alcohol being combusted, and there was no real notable increase. These were just a few of the problems discovered. This method was therefore modified with the use of spirit burners, a lagged copper calorimeter and draught shields to reduce heat loss and also a smaller volume of water was used. These results were slightly more reliable but not particularly accurate, however slight trend can be seen. The results were more reliable as three repeat readings were taken for each alcohol and an overall average of the enthalpy change of combustion taken.

There is an anomalous result seen on graph one involving Butan-1-ol, (which has four carbon atoms in its chain length.) The value I recorded was -673.36KJ/mol where as the value which the line of best fit suggests is -980KJ/mol. This anomaly could be due to several factors the main one I feel could have been a build up of soot on the under side of the calorimeter which meant that the carbon was not fully combusting in carbon dioxide and would not have been accounted for in the results. Reasons such as a draught in the room caused by movements of the other pupils could have had some effect etc. Overall none of these results were particularly accurate which could have been due to heat still being lost into the surroundings, as the draught shields did not fully surround the apparatus. Heat may also have been lost through holes made in the plastic lid to accommodate the thermometer and the stirrer. It would have been a better idea to perform the experiment in a vacuum cupboard. I also did not test for the products that were formed. This means there was no proof that a combustion reaction took place at all. This was just a presumption made due to the chemical equation; other atoms in the air may have also played a part in the reaction. The alcohol may not have been burnt for long enough to allow it to fully combust. Another complication

was that it was hard to measure the temperature, start the stop clock and continue to stir the water simultaneously. This would have therefore increased the human error in the experiment along with the human error produced when measuring the temperature on the thermometer. This % error is stated in my plan.

My final modified method using the flame calorimeter, which was made of glass, was the most accurate. However an anomalous result can be seen on graph two involving Propanol which has three carbon atoms in its main chain. A value of - 1130.656KJ/mol was recorded however the line of best fit suggests a value of - 1360KJ/mol. Performing three repeat readings of each alcohol and taking the overall average may have eliminated this result. However as time and apparatus were limited this was not possible. These results were overall much more accurate and reliable as a definite trend can be seen. The increase in enthalpy change of combustion per carbon atom in the chain length was very similar to that calculated using the bond energy calculations. These results were also closer to that stated in the data book than the they were for the previous method. The apparatus used were more accurate in this method which reduced the amount of systematic error within the method. For example the thermometer used could measure to the nearest half a degree where as in the previous method the thermometer only measured to the nearest degree. The spirit burners containing the alcohols were also measure to three decimal places instead of two as it was in the last method. The % error is calculated below.

Thermometer

$$\% \text{ error} = \frac{0.5 \times 100}{\text{temperature } (^{\circ}\text{C})}$$

Using the results from methanol the starting temperature was 25.5 degrees

$$\begin{aligned} \% \text{ error} &= \frac{0.5 \times 100}{25.5} \\ &= 2.0\% \end{aligned}$$

2% is still quite a large value caused by instrumental error and therefore could be reduced still by using a thermometer which measure to 0.2 of a degree.

The % error for the balance using the initial mass of methanol is,

$$\begin{aligned} \% \text{ error} &= \frac{0.001 \times 100}{14.245} \\ &= 0.007\% \end{aligned}$$

The error produced by the balance is very little and will not be the cause of the inaccuracy in my results

There was also still human error involved in the method when recording the temperature however the slightly more accurate thermometer reduces this.

To conclude from this investigation I have discovered that the enthalpy change of combustion does increase as the carbon chain length within the alcohol increases. The straight chain alcohols have a greater enthalpy change of combustion than that of their isomers with branched chains.

This experiment could still have been improved by repeating three readings for each alcohol. Another improvement to this method would have been to use a data logger to

record the increase in temperature as that would eliminated the majority of the human error that was involved.

References:

1. Cambridge Advanced science, Brian Ratcliff
2. Cambridge Advanced science, Brian Ratcliff
3. Chemistry, R.W. Thomas

Bibliography

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