

THE EFFECT OF HYDROGEN PEROXIDE ON THE HEAT OF COMBUSTION OF ETHANOL

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ABSTRACT

The effect of hydrogen peroxide on the heat of combustion of ethanol has been investigated via thermochemical measurements. The additive (hydrogen peroxide) has been confirmed to enhance the heat of combustion of the pure ethanol sample. The heat of combustion value of pure ethanol sample was obtained experimentally to be -490kJ/mol. With the addition of 0.01 mole of H₂O₂, a value of -500.4kJ/mol was recorded. The heat of combustion was found to increase with increase in the concentration of the additive such that a value of -1129.3kJ/mol was obtained at 0.10 mole concentration of the additive. The mechanism of the interaction of H₂O₂ with the ethanol molecule has been explained through UV-Visible spectroscopy and was attributed mainly to bathochromic and hyperchromic shift.

Keywords: Effect, Hydrogen peroxide, Combustion, Ethanol.

1.0 INTRODUCTION

Combustion is a branch of science and technology that deals with the liberation and use of energy evolved during the reaction of chemical species. In common usage combustion describes the process of rapid heat liberation and is commonly associated with appearance of luminous flame [1]. Combustion is a fast exothermic reaction and it works hand in hand with flames.

Heat release during combustion rates have practical significance since they determine the size of the combustion volume in which the energy transformation takes place. Experiments have shown that flames in potentially combustible mixtures will not propagate unless an adequate initiative source is available [2]. Tedder *et al* [3] observed that the lack of understanding of basic flames reactions was apparent early in this century when the development of the spark-ignited gasoline engine ran into problems with uncontrolled ignition that led to excessive heat transfer, loss of power, occasional engine damage and noise. This problem has been termed knock. There is now a considerable evidence associating the incidence of knock with the auto ignition of the fuel-air mixture ahead of the advancing spark ignited flame front. A solution to the problem was discovered by an engineer and a chemist [4] who added tetraethyl-lead (TEL) to the fuel.

The mechanism of inhibition of cool flame reactions by TEL was not then understood and even today has not been fully elucidated. It is likely to be associated with the breakdown of TEL during the cool-flame reactions to give a 'fog' of finely divided oxides of lead. These solid particles may provide a surface for hydrocarbon chain-termination reaction and hence prevent the second-stage flame-initiation reactions from building up to give ignition. Lead alkyl appears to be unique anti knock agents possibly because the cool-flame reactions themselves provides the necessary energy for the inhibiting process. The proposal mechanism is supported by experiments in the flow reactor described above in which a small addition of TEL to the fuel allowed the cool flame to remain intact but caused the second flame to disappear slowly from the reactor.

Recently, acetone has been reported as an additive to gasoline, which effect is said to lead to increased mileage. This advantage arises due to improvement in the fuel's ability to vaporize completely thereby eliminating the surface tension that causes an increase in particulate vaporization temperature [5]. Acetone can reduce hydrocarbon emissions up to 60-percent. In some older cars, the HC readings with acetone have been observed to drop from 440 to 195ppm [5 and 6].

Ethanol is known to be used as a fuel, either by itself or mixed with petrol in racing cars and in rockets [7]. The present work reports the results of hydrogen peroxide as an additive to ethanol fuel. The report is part of the on-going research in our laboratory towards the discovery of liquid solutes with satisfactory chemical potentials to enhance the quality and performance of gasolines in automobile engines. Elucidation is based on the kinetic and molecular deviations of the sample-additive system from that of the pure sample system.

The authors believe that the research will open another area of interest to approve efficient additive which can enhance the combustion efficiency of our fuels.

2.0 EXPERIMENTAL

2.1 Materials Preparation

Analytical grades of ethanol (C_2H_5OH) and hydrogen peroxide (H_2O_2) were purchased from a chemical shop in Uyo, Akwa Ibom State, Nigeria.

2.2 Determination of Heat of Combustion of Pure Ethanol Sample

A simplified method as reported by Ababio [7] was adopted in our laboratory to determine the heat of combustion of the ethanol sample. The experiment was carried out in a draught-free area. Ethanol ($50cm^3$) was measured into one of the spirit lamps. The initial weight of the lamp with the content was taken and recorded. The lamp was ignited and placed in a fixed distance to raise the temperature of water ($100cm^3$) clamped (with thermometer and stirrer) over the flame, to about $50^\circ C$. The lamp was put off and the combustion system re-weighed to determine the difference.

2.3 Determination of Heat of Combustion of Ethanol Containing Hydrogen Peroxide at Various Concentrations

Hydrogen peroxide ($1.00cm^3$) representing 0.01 mole was measured into a clean measuring cylinder and made up to $50cm^3$ with pure ethanol sample. The mixture was poured into the spirit lamp and the initial weight determined. The lamp was lit to raise the temperature of a pre-weighed water, and the final mass of the

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lamp taken. The same method was followed for 2cm² (0.02 mole) up to 10cm³ (0.1 mole) volume of additive (hydrogen peroxide).

3.0 RESULTS AND DISCUSSION

3.1 Results

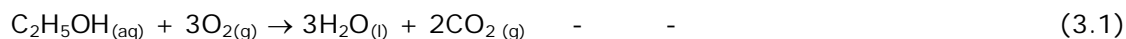
Table 3.1: Heat of Combustion of C₂H₅OH and C₂H₅OH – H₂O₂ mixture

Volume of H ₂ O ₂ used (cm ³)	Concentration of H ₂ O ₂ (mole) added	Initial temp. °K	Final temp. °K	Mass of lamp before combustion (g)	Mass of lamp after combustion	Time (sec.)	Heat of Combustion kJ/mol
0	0.00	301	329	129.3563	128.459	200	490.0
1	0.01	301	329	130.851	130.454	221	500.4
2	0.02	301	329	131.515	130.454	242	509.9
3	0.03	301	329	132.109	131.107	274	539.9
4	0.04	301	329	133.637	132.688	282	570.0
5	0.05	301	329	134.010	133.151	318	629.8
6	0.06	301	329	135.132	134.359	320	700.0
7	0.07	301	329	135.903	135.231	322	805.4
8	0.08	301	329	136.320	135.759	324	964.3
9	0.09	301	329	137.757	137.258	326	1084.1
10	0.10	301	329	138.048	137.569	328	1129.3

3.2 Discussion

3.2.1 Combustion of Ethanol

The combustion of ethanol is essentially an exothermic process with a non-smoky flame, resulting in part or all of the ethanol molecules being converted to carbon (IV) oxide and water vapour according to the equation.



The reaction proceeds via a high temperature free-radical mechanism.

3.2.2 The Effect of Hydrogen Peroxide on the heat of Combustion of Ethanol

The results obtained on the action of the peroxide on the alkanol were recorded in Table 3.1 and depicted in Fig. 3.1. Fig. 3.1 shows the variation of the heat of combustion in different concentrations of hydrogen peroxide. It was observed that the heat of combustion increased with increased concentration of hydrogen peroxide (the more increase in the number of moles of the peroxide, the lower the intensity of the flame), this implies that hydrogen peroxide inhibits the combustion rate of the ethanol sample, consequently enhancing the heat of combustion of the hydrocarbon sample. The heat of combustion value obtained from pure ethanol sample as recorded in Table 3.1 is -490.0kJmol^{-1} , the negative sign signifying that the combustion process was exothermic.

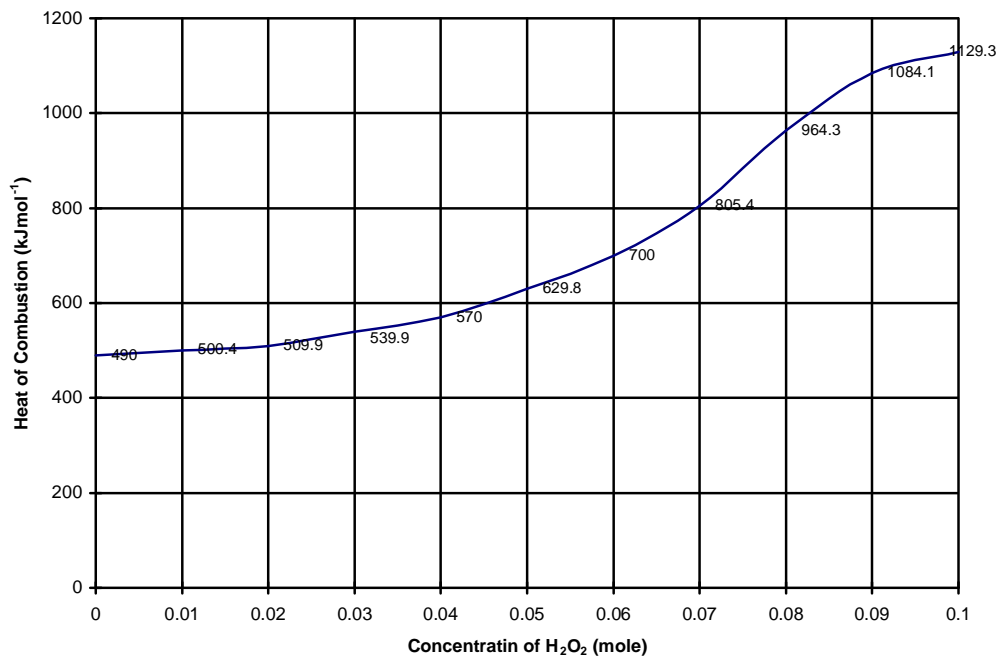


Fig. 3.1: Plot of Heat of Combustion (kJmol⁻¹) versus concentration of H₂O₂ (mole).

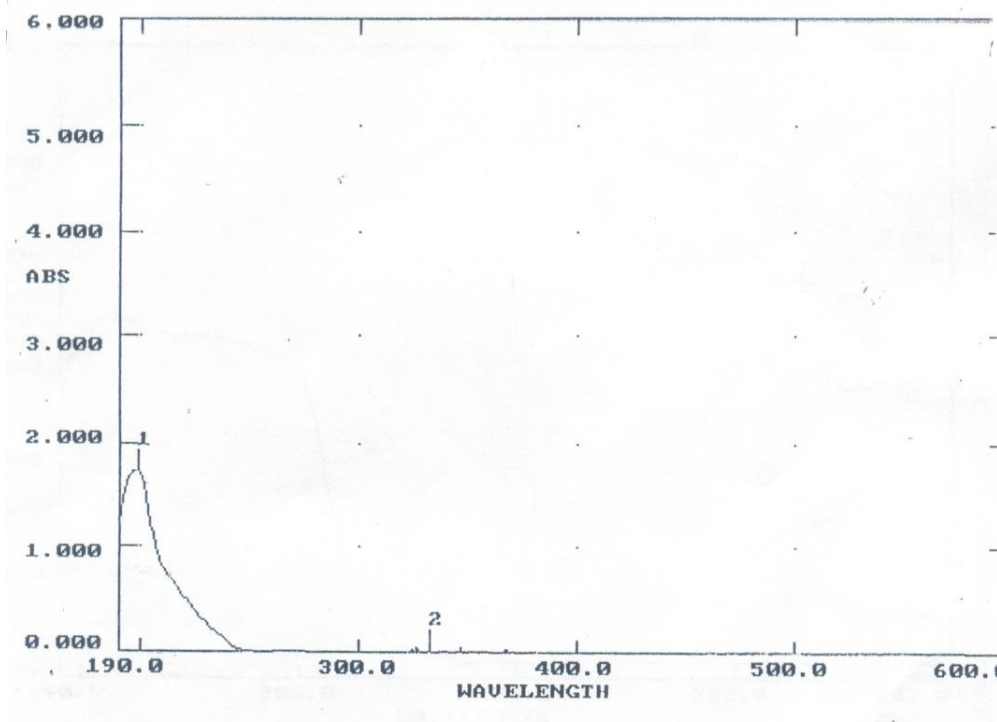


Fig. 3.2: UV-Visible spectrum of pure ethanol sample.

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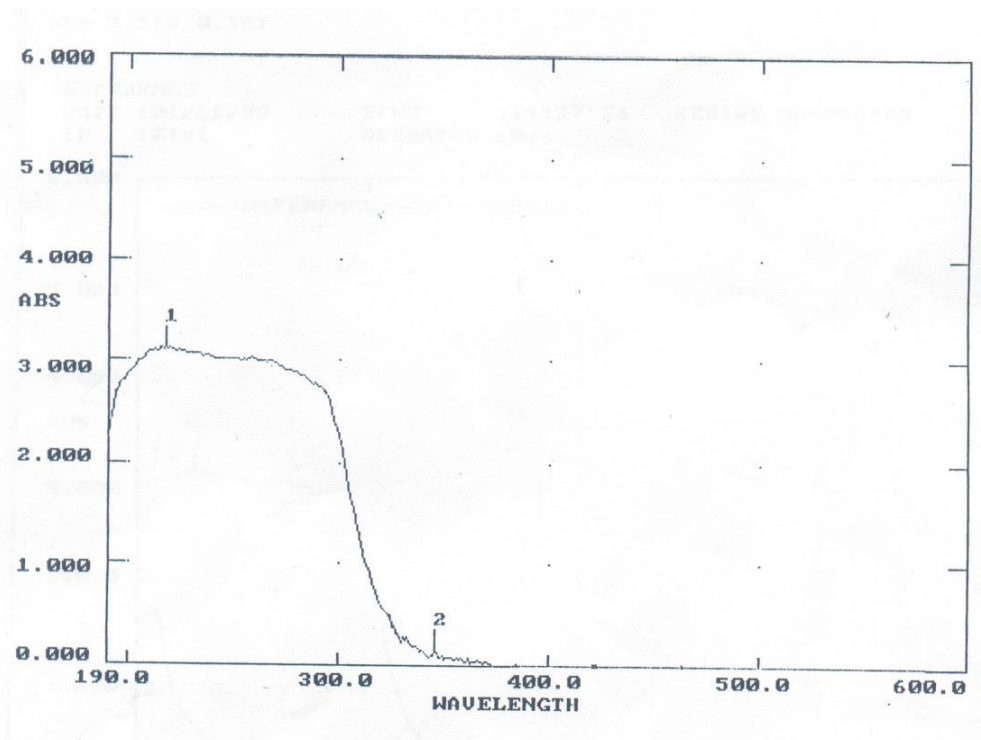


Fig. 3.3: UV-Visible spectrum of pure Hydrogen peroxide.

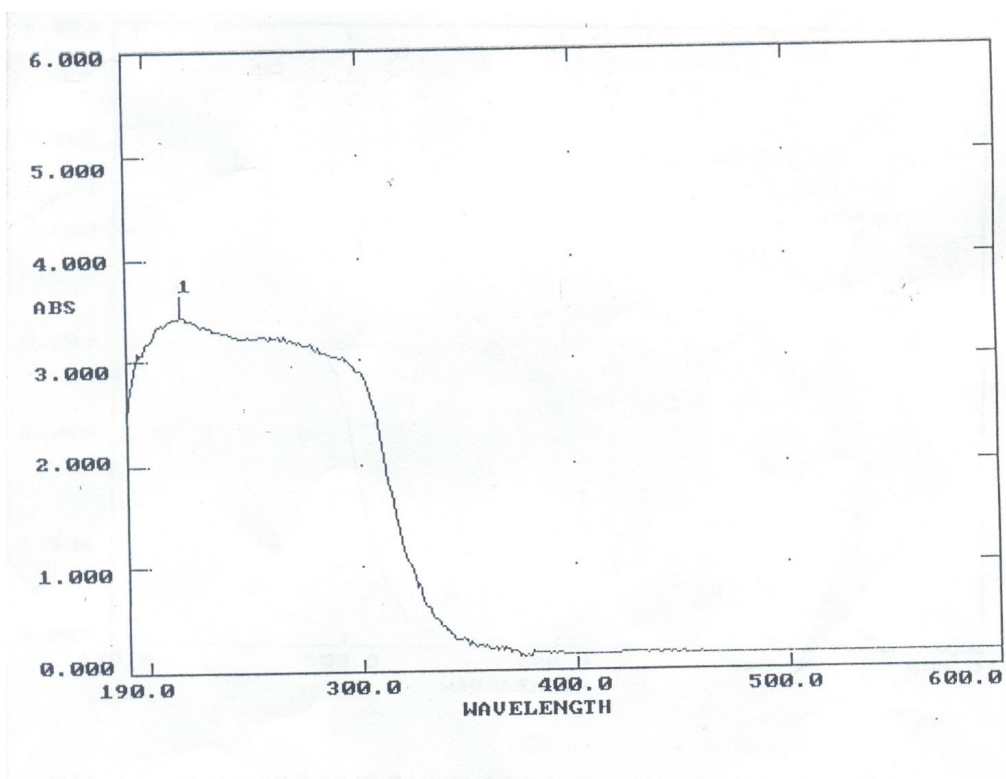


Fig. 3.4: UV - Visible Spectrum of Pure Ethanol Sample with Hydrogen Peroxide.

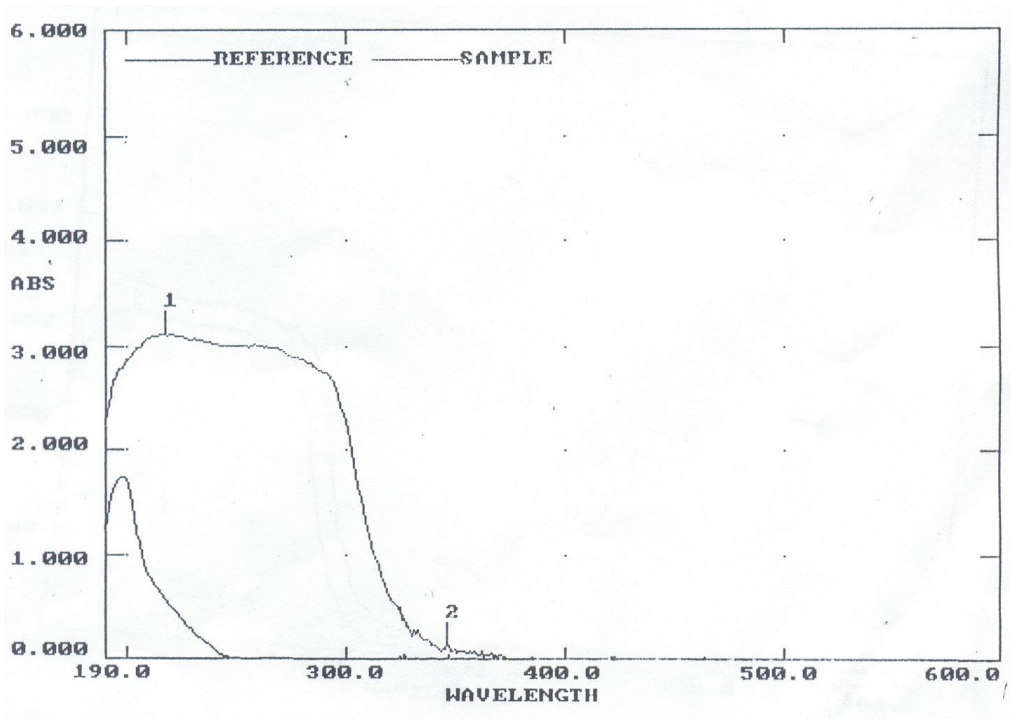


Fig. 3.5: Comparison of mixture with pure ethanol.

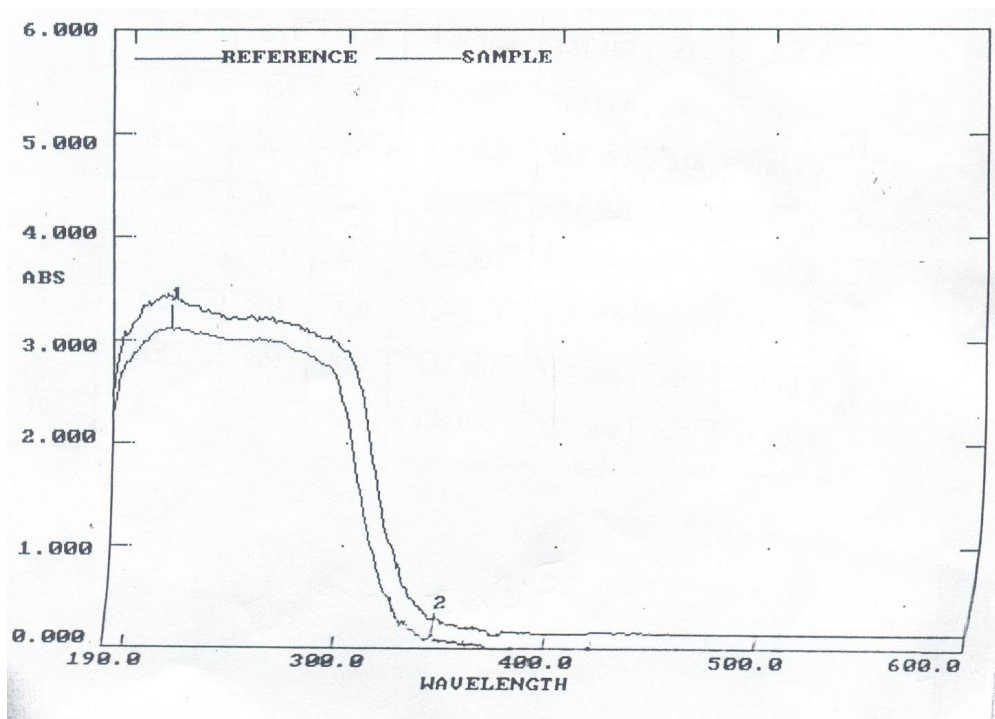


Fig. 3.6: Comparison of additive with mixture (ethanol/hydrogen peroxide).

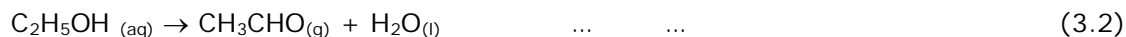
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Higher values of -500.4kJmol^{-1} and -1129.3kJmol^{-1} were obtained upon the introduction of H_2O_2 (0.01 mole and 0.10 mole) respectively. As observed in Fig 3.1, the combustion curve rises gradually and tends to a maximum at a concentration of 0.10 mole of the additive. The increasing values of Heat of combustion with increased concentration of H_2O_2 suggests that more energy is released and thus more work is done by the hydrocarbon mixture than the pure from [8 and 9].

3.2.3 Mechanism of the Action of Hydrogen Peroxide on Ethanol Sample

In order to understand the mechanism of action of H_2O_2 on ethanol, an Ultra-Violet Spectrophotometer (UNICAM β -HEXIOS MODEL) was employed. Fig. 3.2 shows the UV-visible spectrum of the pure ethanol sample under investigation. The spectrum reveals that the pure ethanol sample used absorbs maximally at 199nm, ($\lambda_{\text{max}} = 199\text{nm}$) with a corresponding absorbance of 1.729 (i.e. $\log \epsilon = 1.729$).

This absorption peak agrees well with the expectation as reported by Pavia *et al* [9]. According to the authors, alcohol and amines absorbs in the range 175 to 200nm. The maximum wavelength of 199nm suggests an electronic transition from non-bonding to sigma – anti-bonding orbital (i.e. $n \rightarrow \sigma^*$ transition). However, the spectrum also reveals an unexpected weak absorption peak at a longer wavelength region ($\lambda_{\text{max}} = 333.0\text{nm}$) with absorbance of 0.013. This low intensity peak indicates $n \rightarrow \pi^*$ transition and suggests that the ethanol sample might be undergoing partial oxidation into ethanal in the process of continuous exposure during the experiment.



Pavia *et al* [9] explained explicitly that simple ketones, acids, esters, amides and other compounds containing both π -systems and unshared pairs will show two absorption characteristics viz: $n \rightarrow \pi^*$ transition at longer wavelength ($\lambda_{\text{max}} > 300\text{nm}$ low intensity) and a $\pi \rightarrow \pi^*$ transition. The dual transition, ($n \rightarrow \sigma^*$ and $n \rightarrow \pi^*$) observed in this case, are the characteristics of pure ethanol and partially oxidized molecules respectively. Fig 3.3 shows the uv-visible spectrum of the pure hydrogen peroxide (H_2O_2) used as the additive in this study. The spectrum shows that hydrogen peroxide absorbs maximally at 216.0nm ($\lambda_{\text{max}} = 216.0\text{nm}$) with absorbance value of 3.437 (i.e. $\log \epsilon = 3.437$). further explanations by Pavia *et al* [9] reveals that a single bond of low to medium intensity ($\epsilon = 100$ to 10,000 or $\log \epsilon = 2.0$ to 4.0) at wavelength less than 220nm usually indicate an $n \rightarrow \sigma^*$ transition. Amines, alcohol, ethers and thiols are possibilities provided that the non-bonded electrons are not included in a conjugated system. The structure of hydrogen peroxide reveals no conjugation but clearly shows the presence of sigma bonds with non-bonding electrons due to oxygen atom hence, the possible transition is that of $n \rightarrow \sigma^*$.

Fig. 3.4 shows the spectrum of the mixture of ethanol sample with hydrogen peroxide while fig. 3.5 compares the spectrum of pure ethanol sample with that of their mixture. It is observed that the mixture sample absorbs maximally at higher wavelength and absorbance showing two bonds of medium intensity at $\lambda_{\text{max}} = 218.0\text{nm}$ 3.118 and 0.147. These wavelength correspond respectively to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transition suggesting that the additive (H_2O_2) has probably reacted with the ethanol to form a π -bond system.

Fig. 3.6 compares the spectrum of the additive (H_2O_2) to that of the mixture (ethanol-hydrogen peroxide). It is observed that the mixture sample absorbs maximally at a higher wavelength ($\lambda_{\text{max}} = 218.0\text{nm}$) against a lower value of $\lambda_{\text{max}} = 216.0\text{nm}$ for hydrogen peroxide.

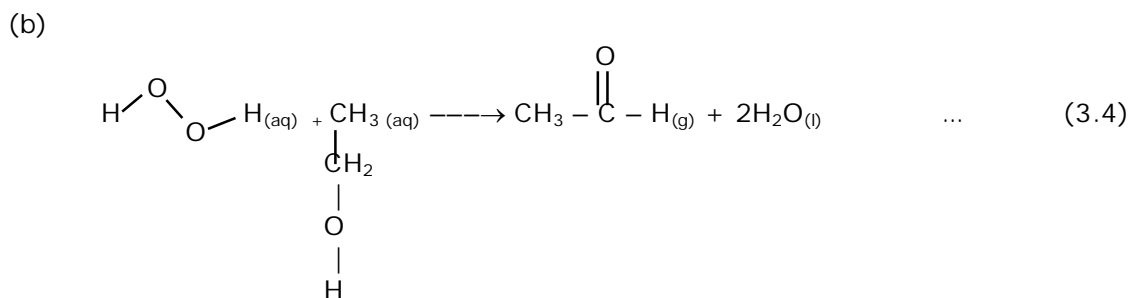
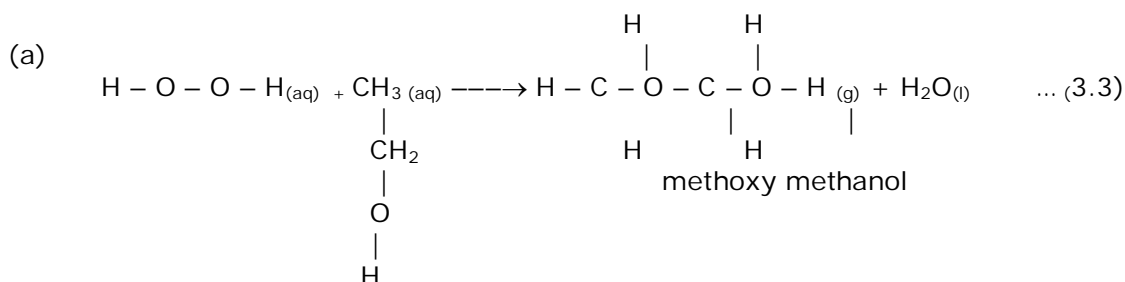
The maximum wavelength value for the H₂O₂ pure sample and that of the mixture are in the same spectral range and indicate an n → σ* transition. This is probably due to the oxygen atoms present in the sigma bond system of the additive and the mixture. However, the presence of a low intensity absorption peaks at λ_{max} = 346.0 with absorbance of 0.147 in the mixture sample (EtOH/H₂O₂) suggests a π-system in the structure of the product as a result of interaction of both molecules.

A careful examination of the spectrum of the reference sample (pure ethanol) and that of the mixture (ethanol + hydrogen peroxide), shows that the additive has led to bathochromic shift (red shift) – a shift to lower frequency or longer wavelength region. There is also a hyperchromic effect (i.e. an increase in the intensity or increase in the absorbance) due to the influence of the additive .

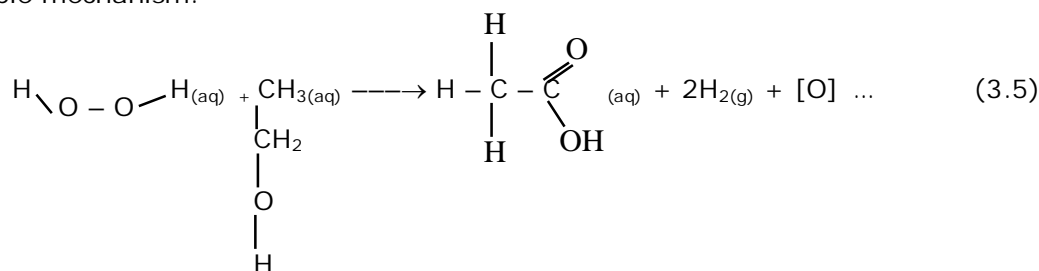
The bathochromic and hyperchromic effects caused by the additive is responsible for the higher heat of combustion values recorded for the mixture.

3.2.4 Proposed Mechanism of the Reaction

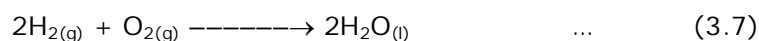
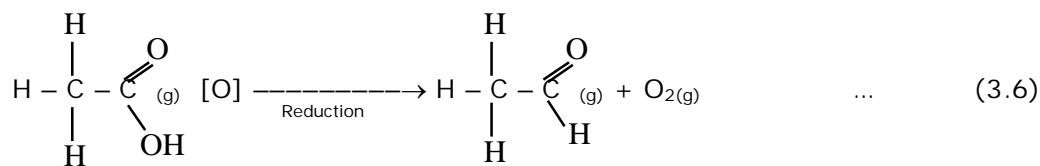
The possible products expected from the interaction of the ethanol molecule with that of hydrogen peroxide are as shown below:



Route (b), Eq 3.4 is a more authentic product due to the presence of the carbonyl group which is probably responsible for the π → π* transition as revealed in the spectrum of the mixture sample. Another alternative route via ethanoic acid finally leads to equation 3.4. This mechanism confirms equation 3.4 as the most probable mechanism.



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4.0 CONCLUSION

Hydrogen peroxide has improved the fuel quality of ethanol thereby increasing the heat of combustion of the hydrocarbon.

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