The role and significance of singlet oxygen in the degradation of engine oils

The Role and Significance of Singlet Oxygen in the Degradation of Engine Oils

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PhD Thesis

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Abstract

The potential role of singlet oxygen in the oxidation, and subsequent degradation, of engine oils was investigated using spectroscopic steady-state and singlet oxygen lifetime measurements. Three currently commercially available antioxidants; a sterically hindered amine (aminic), a sterically hindered phenol (phenolic) and sulfurized olefin, all provided by Lubrizol, were tested alongside previously documented singlet oxygen quenchers; α-tocopherol and squalene.

Singlet oxygen quenching constants, k_Q, were calculated *via* both methods in a polar, 1-butanol, and non-polar, hexadecane, solvents to assess any potential solvent effects on each antioxidant's efficiency.

α-Tocopherol showed the highest quenching in 1-butanol; 2.87×10^8 and 1.19×10^8 $dm^3mol^{-1}s^{-1}$, in both spectroscopic and lifetime testing respectively. Of the commercial antioxidants, the aminic showed significant quenching across spectroscopic and lifetime tests in both solvents; $1.03 – 2.54 \times 10^7$ $dm^3mol^{-1}s^{-1}$ in steady-state and $4.70 – 5.65 \times 10^6$ $dm^3mol^{-1}s^{-1}$ in lifetime tests.

Two different methods were employed to test several combinations of the antioxidants for signs of synergistic or inhibitory behaviour. Of the combinations tested the combination of the aminic and phenolic antioxidants showed the most significant synergistic effects, with improved singlet oxygen quenching across all tests, while the addition of squalene to any of the commercial antioxidants showed little to no sign of synergies in the primary method.

The spectroscopic method was also utilised to attempt to detect signs of chemical quenching by each of the antioxidants. The absorbance of α-tocopherol at 294nm was observed to decrease significantly over the testing period, decreasing by 40-64%, suggesting chemical quenching may be the primary quenching pathway. The phenolic antioxidant also showed signs of chemical quenching; however, further tests are required to confirm the extent of its effect.

Overall it was clear that all three of the commercial antioxidants tested showed the ability to quench singlet oxygen. This coupled with the efficiencies of quenching following the same trend as that seen in internal oxidation tests at Lubrizol; aminic > phenolic > sulfurized olefin, suggests that singlet oxygen may indeed be a factor in the oxidation of engine oils and that measurement of singlet oxygen quenching could be used as a sign of overall antioxidant effectiveness.

Contents

List of Abbreviations

LCAO – Linear combination of atomic orbitals

UV-Vis – Ultraviolet-visible spectroscopy

ε – Molar absorption coefficient

FID – Flame ionisation detector

MB – Methylene blue

RB – Rose Bengal

PDT – Photodynamic therapy

ZnPh – Zinc phthalocyanine

Φ_{Δ} – Quantum yield of singlet oxygen

DMA – 9,10-dimethylanthracene

DPAX – 9-[2-(3-carboxy-9,10-diphenyl)anthryl]-6-hydroxy-3H-xanthen-3-one

DMAX – 9-[2-(3-carboxy-9,10-dimethyl)anthyl]-6-hydroxy-3H-xanthen-3-one

$^1O_2$ – Singlet oxygen

$^3O_2$ – ground state/triplet oxygen

ESR – Electron spin resonance

EPR – Electron paramagnetic resonance

ΔG_{CT} – Change in Gibbs' free energy of charge transfer

HALS – Hindered amine light stabilisers

1. Introduction

1.1. Molecular Orbital Theory[1–3]

Molecular orbital theory is an alternative explanation for how bonds form. This theory suggests that when molecules bond new orbitals are formed, known as the bonding orbitals, which delocalise across the molecule as a whole. This theory provides a more quantitative approach towards bonding, as opposed to the more qualitative approach of valence theory. There are two approximations that are applied to molecular orbital theory, these are orbital approximation and the linear combination of atomic orbitals (LCAO).

The orbital approximation assumes that each electron has its own independent wave function rather than just the overall wave function of the atom or molecule. This allows for the calculation of each wave function using the Schrödinger equation. The LCAO assumes that molecular orbitals are formed by the interference of atomic orbitals with each other, either by the addition or subtraction of one atomic orbital from another.

Each molecular orbital is assigned a label, similar to atomic orbitals, depending on a number of factors.

$$1\sigma_g \qquad\qquad 1\sigma_u^*$$

The number designates the energy level of the molecular orbital, with 1 being the lowest energy level. Next is the designation of the symmetry of the orbital, σ and π are often used the most as they are the first types or orbitals to be formed, much like with atomic orbitals. The letter following, either g or u, are known as parity labels and are again related to the symmetry of the molecule depending on the sign of the axis of the orbital upon inversion, with g denoting no change and u denoting an inversion of the sign. Finally, the * denotes that this orbital is an anti-bonding orbital.

Molecular orbital diagrams can be used to illustrate the energies of bonding orbitals within molecules. They are best suited for simple molecules as the diagrams can become confusing with the addition of too many orbitals. Once the available bonding and antibonding orbitals have been mapped out they are filled using the same principles that govern the filling of atomic orbitals, the Aufbau and Pauli principles. These principles dictate that the orbitals are filled from lowest energy first and that no more than two electrons may fill an orbital, and that if there are two electrons in an orbital they must have opposing spins.

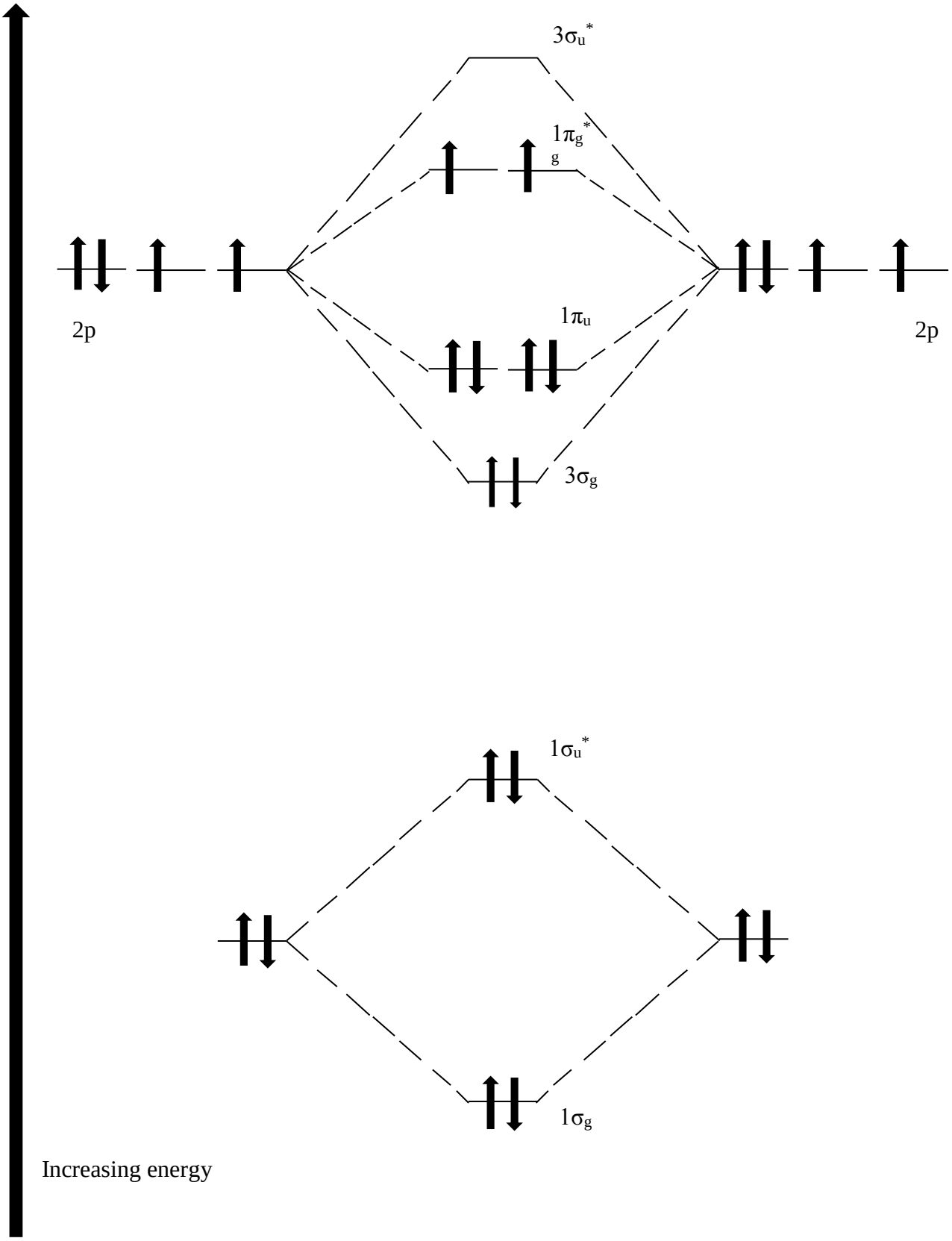

Figure 1 - The Molecular Orbital Formations of Molecular Oxygen

These diagrams can be useful for determining whether a molecule or ion could feasibly exist as well as determining the para- or diamagnetic behaviour of a molecule. This is done by determining the bond order of the molecule. To calculate this using the Lewis model the number of shared electron pairs is calculated. While this method has its merits, there are some situations in which the Lewis model fails to explain the behaviour of certain molecules. A classic example of this is the paramagnetic behaviour exhibited by molecular oxygen, O_2. However, by using the molecular orbital theory model it is possible to explain this.

1.2. Excitation

The excitation of compounds is the primary basis around which singlet oxygen can be formed, a process which will be discussed further in chapter 2. When a molecule or atom absorbs energy, in the case of this study in the form of photons, the electrons become excited and it is possible for them to become 'promoted' to a higher energy state. When this happens the rest of the molecule or atoms needs to react to counter this, in a process known as the Franck-Condon Principle.

1.2.1. Franck-Condon Principle

The Franck-Condon principle states that 'because the nuclei [of atoms] are so much more massive than the electrons, an electronic transition takes place faster than the nuclei can respond'. What this means is that when an electronic transition occurs within an atom the nuclei will begin to vibrate until a new equilibrium inter-nuclear distance is achieved.

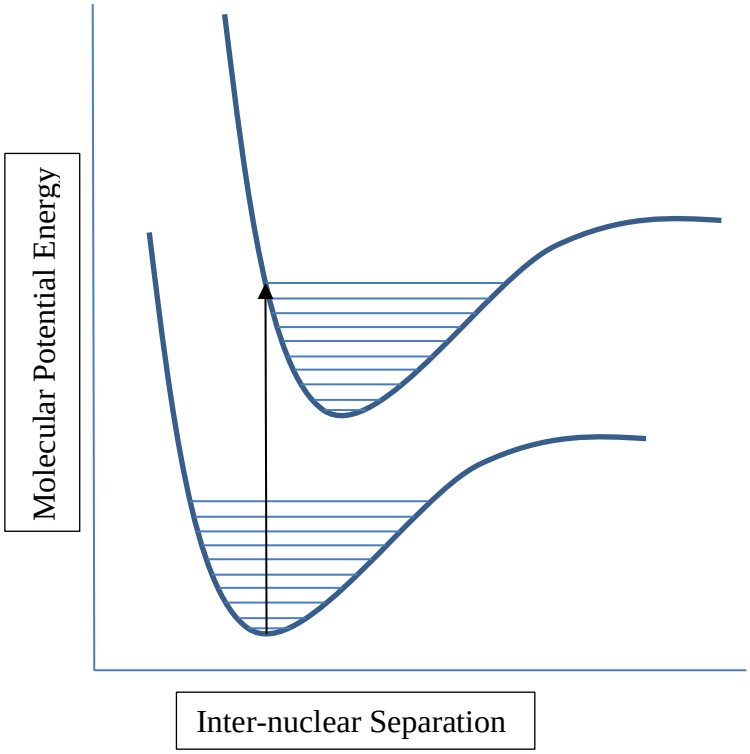

Figure 2 - Illustration of the Franck-Condon Principle Adapted from Chemistry[3 2]

When the transition occurs, the molecular potential energy will not be at its lowest point for the excited state. The energy will decrease and increase again as the inter-nuclear separation shifts, with it eventually reaching an equilibrium distance at the lowest energy point.

1.2.2. Boltzmann Distribution

The Boltzmann distribution can be used to describe the distribution of energy levels of molecules throughout a sample. It can be discerned from the second law of thermodynamics that atoms and molecules have specific energies that they can be at, known as their energy levels. The population distribution of the molecules within a sample will be distributed across all available energy levels at any given temperature, with the lower energy levels being more densely populated than the higher ones unless the temperature is equal to ∞.

As the temperature of a sample is increased so too does the population of the higher energy levels as well as the number of energy levels accessible. The accessibility of these higher energy states increases the reactivity of molecules since the increasing energy also increases the distance of outer electrons from the nucleus, as discussed in the Franck-Condon principle, making it easier for electrons to be transferred.

1.3. Radiative and Non-radiative Transitions[4]

Once a molecule has entered into an excited state it will undergo one of two types of transition to return back to its ground state, these transitions are known as radiative and non-radiative. A radiative transition involves the spontaneous emission of a photon to the surrounding medium and can be observed as either fluorescence or phosphorescence.

However, as the name would suggest, a non-radiative transition does not involve the emission of a photon but rather involves the release of energy in the form of vibration, rotation or translation of the molecule. Most often non-radiative transitions are seen as the electronic energy being released as kinetic energy in the form of heat generation. The potential transitions of a molecule can be expressed using a Jablonski diagram which gives a simplified view of these transitions and their relative energies.

1.3.1. Radiative Transitions

As stated earlier there are two transitions that involves the spontaneous emission of a photon; fluorescence and phosphorescence. Fluorescence is a fast transition which occurs almost instantaneously upon removal of the excitation source, meanwhile phosphorescence is a much slower transition which can continue to occur long after the excitation source has been removed.

When observing a fluorescence spectrum, it can be observed that the excitation and emission spectra are almost mirror images of each other, due to the transitions being the same only in reverse. It can also be noted that the emission spectra will always occur at a longer wavelength that the excitation source. This is due to the fact that some energy will be released as vibrational energy after the initial excitation as the excited state relaxes down the vibrational levels of the excited state before emission occurs. The intensity of the emission can be largely effected by the solvent used as certain solvents, mainly those which have the ability to accept large quantities of electronic energy, can quench the fluorescence.

Phosphorescence is a somewhat more complex transition that fluorescence as it requires certain spin-forbidden transitions to occur first, mainly that of inter-system crossing from a singlet to a triplet state. The intersystem-crossing transition is a non-radiative transition between states of differing multiplicity that requires the separation and conversion of an electron pair from ↑↓ to ↑↑. This is able to occur due to the potential energy of an excited triplet and singlet state intersecting, the probability of which increases in the presence of a moderately heavy atom which can increase the effect of spin-orbit coupling. Once the inter-system crossing occurs the

triplet excited state relaxes back to its lowest vibrational energy state. However, once it reaches this state it is unable to relax any further.

The excited triplet state energy is lower than that of the excited singlet state and as such it is unable to revert back. Also, the transition from the excited triplet state to the singlet ground state is a spin-forbidden transition and as such is very unlikely to occur. This leads to a long potential lifetime for the excited triplet state, something which this project utilises to form singlet oxygen.

As stated earlier, the presence of spin-orbit coupling aids the inter-system crossing transition, and it will also aid in the transition from the triplet to the singlet ground state as this allows the spin-forbidden transition to occur. However, this leads to the transition from the triplet of the ground state to only give off a weak emission, although it may continue to emit for a long period after excitation because of this.

1.3.2. Non-radiative transitions

Transitions which do not involve the spontaneous emission of a photon occur more often in molecules than those that do. These transitions can include, internal conversion, inter-system crossing and energy transfer.

Internal conversion is the simplest form of transition and can be considered simply the relaxation of an excited state back to a lower energy state. For this to occur without the release of a photon however, requires the conversion of the energy into kinetic energy which can then be converted and released as heat.

This project is heavily reliant on the other two of these transitions occurring within the sensitising dye to produce singlet oxygen, these are inter-system crossing and energy transfer.

Inter-system crossing occurs when the potential energy curves of the singlet and triplet states of an atom or molecule intersect. This can allow for the conversion from the excited singlet to the excited triplet state. This transition needs to occur to allow phosphorescence to occur. The transition to the triplet state also increases the lifetime of the excited state since the lowest vibrational state of the triplet is lower than the transition point to the singlet, and the transition from the triplet to the ground state is spin-forbidden. This aids in the production of singlet oxygen as with a longer lifetime there is a higher chance of interactions with molecular oxygen.

The interaction between the excited triplet state and molecular oxygen to produce singlet oxygen is the energy-transfer transitions; where, as the name would suggest the energy is transferred from the excited triplet state to molecular oxygen. This can occur by a few different means, but the primary method is via collision between the sensitizer and molecular oxygen.

1.4. Ultraviolet-Visible Spectrophotometry[2,4–6]

In this project the primary method for measuring the quenching ability of the different antioxidants will be using ultraviolet-visible spectrophotometry (UV-Vis). UV-Vis works on the principle that compounds which have a colour will absorb wavelengths from one area of the spectrum of light while transmitting the others. The transmitted light is what gives the compound its colour. An example of this is the dye methylene blue which has a dark blue colour. When looking at the absorption spectrum for methylene blue it can be seen that it absorbs light in the region of 550-700 nm which lies in the red area of the spectrum.

The transmittance of a molecule can be calculated by taking the ratio of the intensity of the light radiation that passes through the sample to the detector, *I*, and the intensity of the initial radiation released from the source, I_0.

$$\text{Equation 1}$$

The intensity of the transmitted intensity can be related to the path-length, and concentration of the sample tested, by the Beer-Lambert law;

$$\text{Equation 2}$$

Where;

ε – Molar absorption coefficient ($dm^3mol^{-1}cm^{-1}$)

– Cell path length (cm)

– Concentration ($moldm^{-3}$)

The molar absorption coefficient can also be known as the extinction coefficient and is the value of which is dependent on the frequency of the initial radiation and the intensity of the absorbance on the molecule. Therefore, the higher the value of ε the more effective the molecule is at absorbing radiation and the higher the absorbance will be at lower concentrations.

The molar absorption coefficient is also specific to the compound tested and will vary depending on the solvent used

The absorbance of a molecule can be seen as the inverse log of the transmittance and as such we are able to manipulate the relationship between transmittance and absorbance to give;

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ö سي à é ¨Ω ِّ ِ Equation 4

This can then with used with the Beer-Lambert law to describe the relationship between absorbance and concentration.

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Since absorbance is proportional to the concentration of the compound being tested, absorbance can be used to determine the concentration of a solution if other variables are known.

Alternatively, by plotting the absorbance value at various concentrations it is possible to calculate a value for ε from the gradient of the plot, if the path length is also known. However, at very high concentrations it is possible for the relationship to stray from linearity due to instrumental constraints. This will normally occur around the region of absorbance values of 1.5 and higher.

When using UV-Vis spectrophotometry it is important to take into consideration which region you are looking to measure as this will determine what type of cell you can use to measure. Working within the visible section of the spectrum it is possible to use a plastic or glass cell to contain the sample being tested. However, if a measurement is required into the ultraviolet region then a quartz cell must be used as ultraviolet light is not transmitted through glass and plastic cells.

1.5. Laser Spectroscopy[4,7]

Laser stands for Light Amplification by Stimulated Emission of Radiation and has various applications within chemistry; however, the use of lasers most suited to this project is within the realm of spectroscopy. The laser used within this project is a monochromatic laser, in that all of the emitted photons are at the same energy, using neodinium^{3+} ions in yttrium aluminium garnet (Nd-YAG) as the laser medium, which emits at 1064nm.

Lasers operate on a number of requirements, the first of which is the use of an excited state with a long enough lifetime to be able to participate in stimulated emission, which allows for the simplification of the number of photons emitted at the energy of the laser medium's transition energy. For this the principle of population inversion, in which the population of an excited state is greater than that of the ground state, is used.

To achieve population inversion a laser medium with either a three or four level energy arrangement is put into an excited state via an electrical discharge or a high-intensity flash of light, a process known as pumping. From here the excited state rapidly transitions, via a non-radiative transition, to a lower energy state which will then either slowly transition down to the ground state, in a three-level arrangement, or another lower energy state, in a four-level arrangement, during which it will spontaneously emit a photon. The transition from the excited state to the ground state or to the lower excited state is known as laser action. The advantage that the four-level arrangement has over the three-level arrangement is that initially there is zero population in the lower excited state, therefore any population in the higher excited state leads to population inversion, where as in a three-level arrangement a significant portion of the ground state has to be excited before this occurs.

1.5.1. Laser Cavity

The excitable laser medium is held within a cavity which ensures that the photons generated in significant quantities have a specific frequency, direction of travel and state of polarization.

1.5.2. Pulsed Radiation

There are two main methods of creating pulsed radiation from a laser; Q-switching and mode locking. Q-switching allows for pulses of radiation down to 1ns durations to be formed, while mode-locking is able to achieve pulses below 1ps in the right circumstances. Both rely on modification of the resonant characteristics of the laser cavity to achieve pulses of radiation.

For Q-switching the resonant characteristics of the cavity are hindered in a way that allows for a build-up of a population inversion without stimulated emission, before being applied to the cavity and causing a sudden burst of stimulated emission. This can be achieved by the use of a Pockels cell or a saturable absorber. Pockels cells work by converting the emitted photons which are polarized along one plane to being reflected in a perpendicular plane, thus preventing them from causing further stimulated emission. It is activated by applying an electrical potential difference across the cell, but upon removal of this the energy stored within the cavity can cause a sudden, intense burst of stimulated emission.

Mode-locking allows for even shorter pulses of radiation, the length of which is dependent on the resonant characteristics of the cavity, and more so on the number of modes that can be trapped within it. Modes will normally have random phases relative to each other, but by locking these phases it is possible for the modes to interfere with each other, giving rise to short, sharp peaks of radiation. The sharpness of these peaks is determined by the range of modes that occur, the wider the range, the narrower the pulses produced. Mode-locking is achieved by varying the Q-factor of the cavity at intervals of ώ͂ς ü This only allows photons that are able to make the round-trip of the cavity within this time period to be amplified.

1.5.3. Application of Laser Technology in Chemistry

There are a number of applications that have been found for laser both in and outside the realm of chemistry. However, the introduction of laser technology helped make vast improvements within spectroscopy, their properties allowing for measurement of previously unobservable transitions as well as improving on already established spectroscopic techniques.

1.5.3.1. Multi-photon Spectroscopy

The ability of lasers to initiate multiphoton transitions in molecules without a change in parity, g → g and u → u transitions. This is something that was previously unobservable by previous spectroscopic methods which were only able to observe single photon transitions involving a change in parity, g ↔ u.

1.5.3.2. Raman Spectroscopy

One of the spectroscopic methods that has been improved upon by the addition of laser techniques is that of Raman spectroscopy. The intensity of the laser radiations lead to an increase in the intensity of the scattered radiation, thus increasing the sensitivity of the

technique. The definition of a laser beam also leads to greater precision due to a decrease in the probability of stray scattered light. The monochromatic nature of laser radiation also allows for higher resolution.

1.5.3.3. Time-resolved Spectroscopy

By utilising pulsed-beam techniques it is possible to observe the transitions of reactions as they occur. Q-switched pulses can be used to observe reactions that are diffusion controlled, while mode-locking techniques can be utilised to observe the transitions from the conversion of energy within molecules.

1.5.3.4. Precision-specified Transitions

The ability to select specific wavelengths to excite molecules at with high intensity allows for the selection of specific states to excite within molecules. This has been shown to be useful in the enhancement of certain reactions that would otherwise only proceed at high temperatures.

1.5.3.5. Isotope Separation

Given the fact that each isotope of a molecule will absorb at slightly different wavelengths to each other, along with the fact that lasers are able to operate at specifically discrete levels, allowing for the excitation of only one of the isotopes. This excited state can then be ionised and its behaviour observed, this process being known a photoionization.

Another method of isotope separation utilising lasers is known as photodissociation. This method utilises either two separate lasers or a multiphoton process. The first step being to use discrete excitation to excite the desired isotope and then a continuum of laser radiation to cause dissociation.

Two other methods of isotope separation include photoisomerization; the conversion to one specific isomer upon absorption of specific wavelengths, and photodeflection; observation of the recoil of an atom upon transfer of the exciting photon's linear momentum.

1.5.4. Types of Lasers

Different types of laser lend themselves towards certain applications, with each having their own advantages and disadvantages of use. Some examples of the different types of lasers will now be discussed.

1.5.4.1. Gas Lasers

As the name would suggest gas lasers use a gas as the laser medium. In most cases two gases, or two variations of a gas, are used within the laser cavity; one for pumping and one for the laser emission. Some examples of gas lasers include nitrogen lasers, helium-neon lasers and argon ion lasers, which use the Ar^{+} and Ar^{2+} ions.

The main benefits of gas lasers are their ability to generate very high power beams which is partially due to the fact that they can be cooled very efficiently and are therefore less likely to be affected by overheating.

1.5.4.2. Chemical or Exciplex Lasers

Chemical lasers utilise chemical reactions which produce molecules with inverted populations rather than just exciting the molecule to induce the inversion. Exiplex lasers work similarly in that they produce an inverted population by the formation of a product, however in this case the population inversion is due to the fact that the lower state does not technically exist. The exiplex can only form in the excited state and it is the dissociation of this excited state once the excitation energy is removed that leads to the laser radiation.

1.5.4.3. Dye Lasers

Dye lasers operate as standard lasers with a dye molecule in the solvent as the laser medium. Dye lasers are highly useful for certain situations due to the fact that they can be continuously tuned and retuned with ease. This allows for dye lasers to be used to scan across a range of wavelengths within a run. An example of a dye laser medium would be rhodamine 6G dissolved in methanol[7].

1.6. Gas Chromatography

Chromatography is a very useful analytical technique for separating out components in samples that contain multiple compounds. Within the scope of this project gas chromatography was tested for use in attempting to detect potential by-products that may arise from chemical quenching of singlet oxygen, if it is occurring.

Gas chromatography works by injecting a sample into a heated chamber which vaporizes the sample into gaseous form which then mixes with an inert carrier gas, most commonly either nitrogen or helium, known as the mobile phase. The gas will then travel through the

chromatography column which is coated with a compound, known as the stationary phase, and housed inside an oven; this is where the separation of the sample occurs. The time it takes each component of the mixture to travel through the column will vary depending on how strongly it interacts with the lining of the column.

This allows for some levels of tuning of the separation depending on what potential interactions the components might have, for example changing the polarity of the compound used in the column should cause non-polar compounds to travel through faster than polar compounds, due to increased likelihood of interactions between polar compounds and the polar stationary phase. It should also be noted that small compounds will also pass through faster than larger compounds due to there being a lesser chance of collisions with the column material and therefore less chance of interactions occurring.

The advantage of gas chromatography as a separation technique is that it can be used with very small sample sizes, down to µl, so it would be possible if desired to take multiple samples from an irradiation sample at different times to look for any discrete change. Another advantage of gas chromatography is the types of detectors that can be used. The detector most commonly used in conjunction with gas chromatography is a flame ionization detector (FID), which combusts the sample as it exits the column causing the compound to become charged. The charged compound is then attracted to one of two nearby electrodes depending on the charge, producing an electrical current which can be detected.

Another potentially useful detector to use with the gas chromatography would be a mass spectrometer as this could be used to give information to help identify and by-products that may have formed.

2. Singlet Oxygen

2.1. What is Singlet Oxygen?

Molecular oxygen is a rather interesting molecule within chemistry thanks to its unique properties. The main of which is the fact that it forms with a triplet ground state as opposed to a singlet ground state as is common with most other molecules. This phenomenon is caused by molecular oxygen having its two bonding electrons occupying different orbitals with parallel spins.

This can be explained using Hund's maximum multiplicity rule[2] which states that an atom in its ground state will opt to a configuration which yields the highest number of unpaired electrons. This follows with the quantum mechanical idea of spin correlation in that electrons will parallel spins favour staying apart as to lessen the repulsion effect on each other, thus allowing an atom to 'shrink' and increase the effect of electron-nucleus interactions.

There are two singlet states that molecular oxygen can be excited to with relative ease, $^1\Delta_g$ and $^1\Sigma_g^+$, which lie at 98 and 158 kJmol^{-1} above the ground state respectively. As one of the electrons is excited it will change spin so that the bonding electrons have opposite spins. If enough energy is used to excite the electron it may remain in the orbital it was originally in, giving rise to the $^1\Sigma_g^+$ state. However, the $^1\Sigma_g^+$ state has a short lifetime, 7 to 15s in the gas phase[8] and 10^{-11} to 10^{-9}s in solution[9]. Therefore, it can be difficult to try and observe the $^1\Sigma_g^+$ state during reactions.

The $^1\Delta_g$ state, on the other hand, has a much longer lifetime compared to the $^1\Sigma_g^+$ state. This is due to the fact that the transition from the $^1\Delta_g$ state to the $^3\Sigma_g^-$ ground state is considered to be 'spin-forbidden' according to spin selection rules[4]. However, as this transition is considered to be 'spin-forbidden' it is difficult to excite molecular oxygen from its ground state to the singlet excited state that is easiest to work with. Instead the more frequent method of production for the $^1\Delta_g$ state is via relaxation from the $^1\Sigma_g^+$ state since the $^1\Sigma_g^+$ Ą $^1\Delta_g$ transition is not considered to be 'spin-forbidden'.

Figure 3 shows the general configuration of the bonding outer electrons for molecular oxygen in the ground state as well as the two lowest excited states.

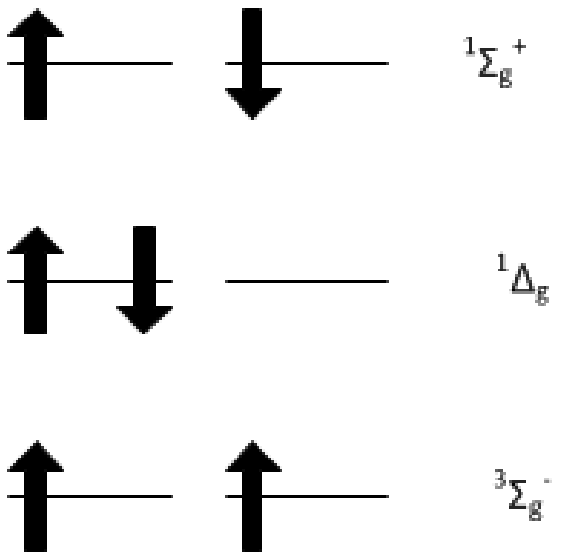


Figure 3 - Illustration of Oxygen Molecular Bonding Orbitals at the Different States[10]

As stated earlier the transition between the $^1\Delta_g$ state and the $^3\Sigma_g^-$ ground state is considered to be 'spin-forbidden', however, this does not mean that the transition cannot occur. The relaxation of the $^1\Delta_g$ state to the $^3\Sigma_g^-$ ground state can be observed in the near-IR region, around 1268nm via both absorption and emission spectroscopy[11]. The signal for this transition is weak but still detectable under the correct circumstances and as such is the basis for lifetime detection of singlet oxygen.

2.2. Generation of Singlet Oxygen

There are a number of different methods for generating singlet oxygen which will be discussed in this section. However, the most prominent method, and the one focused upon throughout this research, is photosensitized production of singlet oxygen.

2.2.1. Photosensitized Production

Photosensitised production is a relatively simple method as it only really requires three components; oxygen, light (of an appropriate wavelength) and a photosensitizing dye. The process relies on the transfer of energy between a previously excited dye compound and molecular oxygen. It is widely regarded as the most preferable method of singlet oxygen production due to its simplicity, efficiency and the control it allows the user over production due to the wide variety of photosensitizers available[12]. This method relies on the use of a dye compound which fits certain criteria, discussed later, to allow it to react with molecular oxygen to produce singlet oxygen.

To be able to produce singlet oxygen the photosensitizer must first enter into an excited state via absorption of light radiation, either via natural light or a specific source such as an LED lamp, thus causing a transition of the molecule from its ground state, S_0, to an excited singlet state, S_n. This excited singlet state will naturally 'relax' down to the lowest excited singlet state, S_1, which is then open to inter-system crossing to yield the lowest excited triplet state, T_1. This triplet state is easier to react with as its lifetime is significantly higher than that of the lowest singlet state, μs vs ns[10]. These transitions are outlined in Equation 3 below as well as in Figure 2.

Equation 6[10]

Where;

P – Photosensitizer

S_0 – Singlet ground state

S_1 – First excited singlet state

T_1 – first excited triplet state.

k_{isc} – rate constant for inter-system crossing.

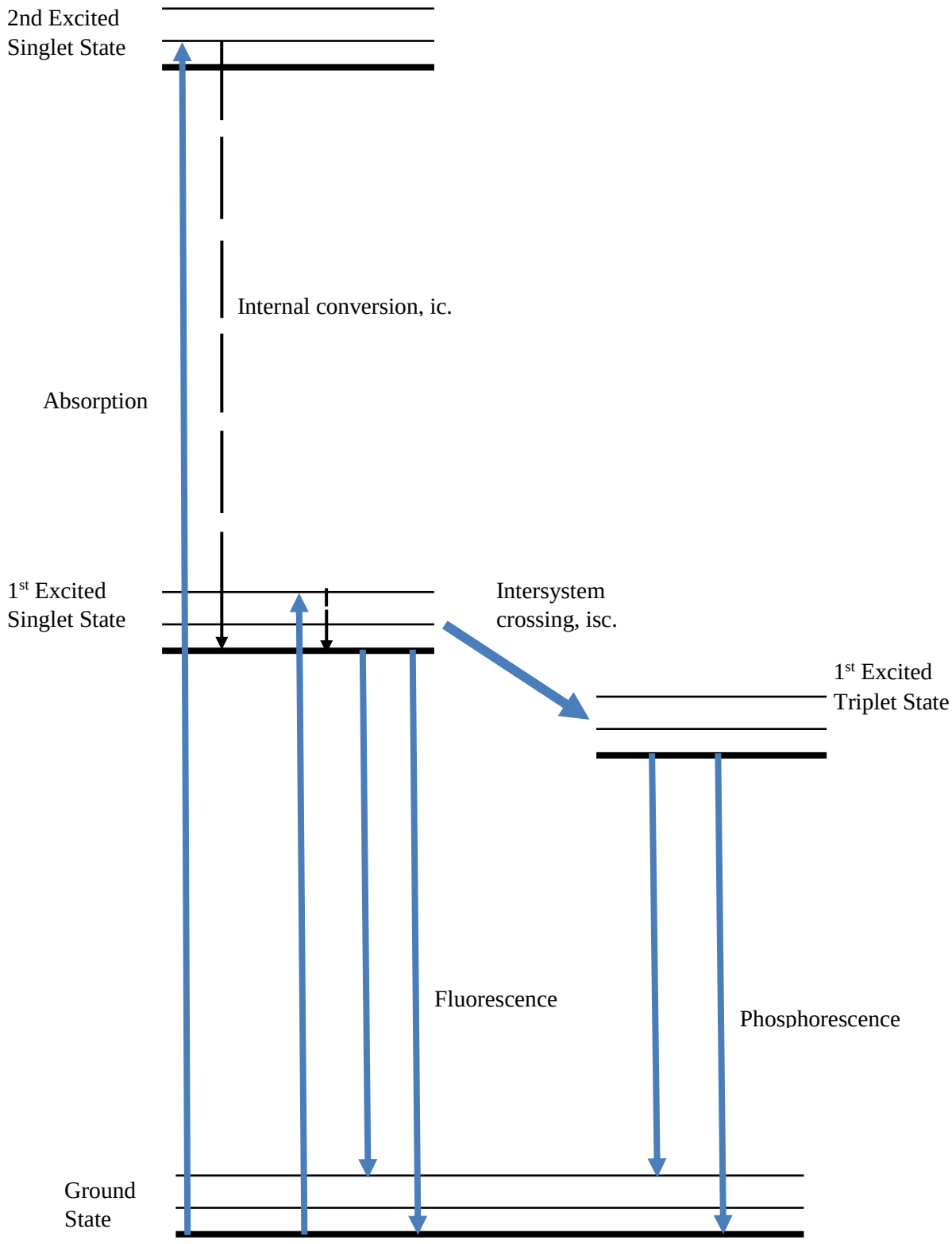


Figure 4 - Possible Transitions from and back to the Ground State

The excited triplet state can then go on to react via two different mechanisms, known as type I and II[13].

Type I involves the production of free radicals via hydrogen atom abstraction or electron transfer with another substrate in solution. It is possible for these free radicals to go on to produce other reactive oxygen species, such as the superoxide radical $\cdot O_2^-$ which will be discussed later. While it is possible to yield singlet oxygen via this mechanism it is not a desirable production method for singlet oxygen as it is unpredictable in its production.

The type II mechanism revolves around reaction between the excited photosensitizer and molecular oxygen via energy transfer which yields singlet oxygen. This is the preferred mechanism for singlet oxygen production as it is reliable and far more efficient than the type I mechanism.

There are certain conditions that need to be met by the photosensitising dye for it to be an effective means of producing singlet oxygen. The first requirement is for the sensitising dye to have a suitably high absorption coefficient in the region of the light spectrum being used, preferably from within the visible or near-visible regions of the spectrum as these are fairly easy and cheap to control.

Secondly, the excited state, often a triplet state obtained via inter-system crossing, needs to be produced in enough quantities for there to be a high enough chance of reaction between the sensitizer and molecular oxygen. This is known as the quantum yield of the triplet state, Φ_T, a value above 0.4 is often desired for sufficient singlet oxygen production. Similar to this requirement, the produced excited state needs to be of sufficient energy to allow for excitation of molecular oxygen, $E_T > 98 kJmol^{-1}$, as well as a sufficient triplet state lifetime, preferably $\tau_T >$ µs, to maximise the chance of reaction.

A high level of photo-stability of the dye molecule is also desirable as this allows for multiple uses of the same dye molecule to produce singlet oxygen with little to no degradation. Preferably each photosensitizer molecule should be able to produce anywhere between 10^3 and 10^5 molecules of singlet oxygen before degrading to a point where it can no longer produce any.

The proportion of the excited triplet state that goes on to produce oxygen is known as the quantum yield of singlet oxygen formation and is denoted as ϕ_{Δ}. Methods for measuring this will be discussed later in this chapter.

2.2.2. Types of Photosensitizer

As long as the dye meets the requirements listed above it is possible to be used as a photosensitiser for the production of singlet oxygen. However, there are a number of different types of dye which may do so, each with their own limitations and requirements.

2.2.2.1. Organic Dyes and Aromatic Hydrocarbons

Three well-known organic dyes used for singlet oxygen photosensitisation are rose bengal, eosin and methylene blue (Table 1). All three of these dyes absorb light within the visible region of the spectrum and have suitable triplet energy states, along with significant triplet state quantum yields ($^{1}_{\Delta} > 0.5$), making them suitable candidates to facilitate singlet oxygen production. All three of these dyes were considered for use during this research because of their effectiveness and ease of use.

Table 1 – Photophysical Properties of Some Common Dyes[14]

Dye	Triplet energy E_T (kJmol^{-1})	φ_{Δ} (aqueous)		φ_{Δ} (EtOH)	φ_{Δ} (CH_3OH)
		D_2O	H_2O		
Rose Bengal	175.85	0.76	0.75	0.68	0.76
Fluorescein	197.62		0.03	0.03	0.1
Eosin blue	190.50		0.52	0.37	
Methylene Blue	133.98			0.52	0.5
Erythrosin blue			0.63	0.69	

2.2.2.2. Methylene Blue

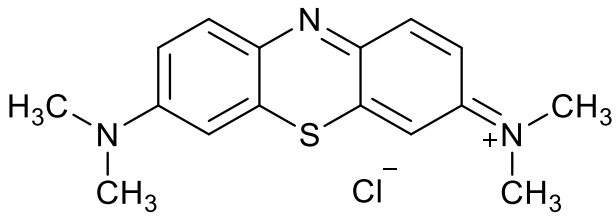


Figure 5 - Chemical Structure of Methylene Blue[15]

Methylene blue (Figure 5) is a phenothiazinium dye which absorbs strongly in the 550-700nm region of the visible spectrum. It has a quantum yield of ~ 0.52[14] which, while not high like some of the other photosensitizers discussed, is high enough to be a suitable sensitizer for singlet oxygen in this study.

However, there are a few potential drawbacks when considering methylene blue for this research, the main of which is its preference towards polar solvents and its hydrophilic nature. Given that this research is trying to focus towards an oil based scenario this is a significant issue.

Another potential drawback of methylene blue is that it is possible to be reduced to form leuco-methylene blue in the absence of sufficient oxygen[16]. Since leuco-methylene is colourless this could affect singlet oxygen production since it would first need to be re-oxidised to methylene blue before it could be excited into the triplet state allowing for singlet oxygen production.

2.2.2.3. Rose Bengal and Eosin

Both rose bengal and eosin are xanthene dyes which are built up from a xanthene skeleton (Figure 6). Xanthene dyes can be especially useful in singlet oxygen production due to the ability to manipulate the xanthene skeleton to alter its photochemical properties. An example of this is by the addition of, or increase in atomic number of, halogen atoms to the xanthene skeleton.

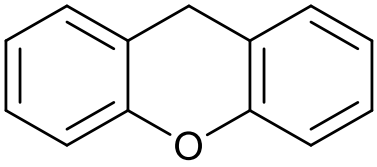


Figure 6 - Chemical Structure of the Xanthene Skeleton[17]

The addition of halogens to the skeleton, especially ones of higher atomic mass, causes a red shift in the peak max of the compound. Being able to 'tune' the compound in this manner can be especially useful if there are constraints on the wavelengths of light that can be used to facilitate singlet oxygen production, such as can be the case with photodynamic therapy (PDT). The addition of the heavier halogens can also lead to an increase in the efficiency of intersystem-crossing of the molecule, therefore potentially increasing its efficiency as a photosensitizer.

As stated earlier both rose bengal (Figure 7) and eosin Y (Figure 8) are examples of xanthene dyes, each showing high absorptions between 480 and 550nm in the visible spectra. The four iodine atoms attached to the xanthene skeleton in rose bengal allow for its high quantum yield; $\Phi_\Delta = 0.75$ (in H_2O) and $\Phi_\Delta = 0.68$ (in ethanol). Meanwhile the bromine atoms in the eosin Y molecule also allow for a high quantum yield; $\Phi_\Delta = 0.8$ (in H_2O) and $\Phi_\Delta = 0.56$ (in methanol).

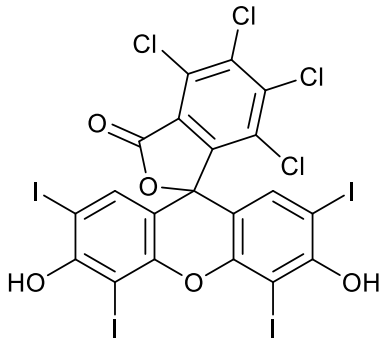


Figure 7 - Chemical Structure of Rose Bengal[18]

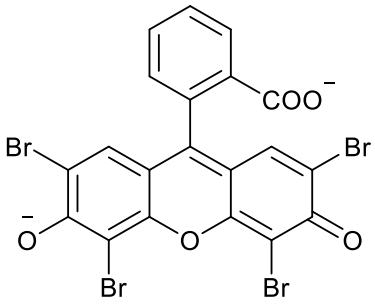


Figure 8 - Chemical Structure of Eosin Y[19]

2.2.2.4. Aromatic Hydrocarbons

Other aromatic compounds; such as naphthalenes, anthracenes and biphenyls, have also been known to be used as photosenstisers. However, there are certain factors that need to be considered in regards to their use. When considering biphenyl compounds there is the potential for strong competition between charge transfer interactions and the energy transfer pathway for singlet oxygen production which can hinder the sensitizer's efficiency. This can be affected by altering the oxidation potential of the substituents on the phenyl rings leading to a change in the free energy of charge transfer, $\Delta G_{CT.}$ By increasing the oxidation potential it is possible to increase the fraction of the triplet state produced that will yield oxygen when quenched by oxygen due to a preference towards the energy transfer pathway.

2.2.2.5. Quinones

Quinones are another group that have proven to be effective photosensitizers for singlet oxygen and are considered an important asset in biological processes[20]. Guiterez et al. obtained values for the quantum yields of singlet oxygen from a number of quinone and anthroquinone derivatives. They found these compounds to be very effective sensitizers, especially in aprotic solvents ($^{1}_{س}$= 0.69 for anthroquinone-2-sulfonic acid and 1,8-dihyroxyanthraquinone). However, water soluble quinines have also been shown to have reasonable singlet oxygen production ability[21].

Quinones were also found to show moderate quenching via physical deactivation [20], although this can be a hindrance if using a quinone as a photosensitizer when trying to calculate the singlet oxygen quenching rates for another compound.

There has been significant interest in one group of quinones found in natural pigments, 3,10-dihydroxy-4,9-perylenequinones. This group includes hypocrellin compounds which have

been researched as possible photosensitizers for the photodynamic treatment of cancer, PDT[22], hypocrellin B for example has shown to have a Φ_{Δ} value of 0.76. However, the major issue with these as photosensitizers is that they have little absorption at wavelengths below 600nm therefore limiting their applicability. This issue has been combated by devising amino derivatives which have shown significantly enhanced absorption in the red spectrum and suitable singlet oxygen generation[23].

2.2.2.6. Porphyrins, Phthalocyanines and Related Tetrapyrroles

Many of the dyes from these groups of compounds meet the basic requirements for use as singlet oxygen photosensitisers. These dyes tend to absorb strongly at several wavelengths within the UV-visible spectrum and have high triplet state lifetimes; leading to a tendency towards high singlet oxygen quantum yields. These dyes also allow for manipulation of the substituents of these compounds to change their properties, thus allowing for tuning towards specific conditions.

2.2.2.7. Porphyrins

Porphyrins dyes are of particular interest for their potential use as singlet oxygen photosensitsers within biological systems, such as during PDT for cancer. This is primarily due to many of the dye from these groups having little to no cytotoxicity in the absence of suitable light radiation, therefore making them optimal for targeted destruction of tissue by only applying the light source in the desired location.

However, one of the major benefits of these dyes for use in biological systems is also its largest hindrance when looking at their use for industrial systems, this is their tendency to undergo rapid photo-bleaching. This property allows these dyes to break down quickly when they are no longer needed within the body, but also means that they would have to frequently be replaced in an industrial setting, which could lead to higher running costs which would be unnecessary if using a dye with better photo-stability.

Examples of some possible substituents of porphyrins along with their specific photophysical properties are shown in Table 2.

Table 2 – Photophysical Properties of Some Metalloporphyrins[14,24]

Complex	φ_T	τ_T (μs)	φ_Δ
H_2TPP	0.82	1380 (300K)	0.63 (C_6H_6)
MgTPP		1350 (300 K)	0.62 (C_6H_6)
ZnTPP	0.88	1200 (300 K)	0.83 (C_6H_6)
CdTPP		260 (300 K)	
PdTPP	1.00	380 (300 K)	0.88 (C_6H_6)
ZnOEP		57000 (77 K)	
PdOEP	1.00	300 (300 K)	

A study by Tanielian *et al.*[12] determined the quantum yield of singlet oxygen and the yield of intersystem crossing for a number of photosensitizing dyes. They found that for dyes which did not show any quenching of fluorescence, such as methylene blue, the singlet oxygen yield was almost 100% efficient. However, it was also found that for dyes which did show fluorescence quenching, such as tetraphenylporphine, the quantum yield of singlet oxygen was greater than the intersystem crossing yield. This was thought to be due to triplet state oxygen catalysis of intersystem crossing of the singlet state.

Jeong-Hyon *et al.*[25] investigated the effect of substituting one or more of the pyrrole rings in tetraphenylporphyrins with a furan and/or thiophene on its photophysical properties and singlet oxygen generating efficiencies. This study found that by changing a pyrrole to a thiophene increased the singlet oxygen quantum yield due to enhanced spin-orbit coupling causing increased rates of intersystem crossing. However, they also found that for the mono furan-substituted compound the quantum yield of singlet oxygen was reduced and noted that this was due to enhanced internal conversion.

Fernandez *et al.*[26] also conducted experiments into singlet oxygen generation by a variety of sensitizers, this time in a pH 7.4 phosphate buffer containing 1% Triton X-100. The samples

were irradiated using a xenon arc lamp and the photosensitization of lysozyme was used as an internal actinometer. This photosensitization is the type of technique that will be used in this project. The values obtained in this study were congruent with others obtained with similar conditions but involving different measurement techniques. An example is the singlet oxygen quantum yield value obtained for mesotetra-(4-sulfonato-phenyl)porphine (TPPS), ρ φ πθ سي س while is a study by Spikes[27] where an O_2 uptake measurement technique was used.

2.2.2.8. Phthalocyanines

The phthalocyanine group of dyes are derivatives of the porphyrins, with their main difference being the nitrogen atoms linking the pyrrole units of the molecule. They tend to exhibit a strong absorption within the red spectra, which makes them potentially useful for biological applications. As with the porphyrins, it is also possible to manipulate the photophysical properties of phthalocyanines in a similar way. Studies have shown that metalphthalocyanines containing diamagnetic metals tend to have higher triplet lifetimes, and therefore higher singlet oxygen quantum yields, than those containing paramagnetic metals, which sometime exhibit little to no quantum yield[24,28].

Also, by altering the substituents or the axial ligands bound to the metal, it is possible to manipulate the hydrophilic or phobic nature of the compound, thereby allowing the user to exert a level of control over the localisation of the dyes within a system; something that is especially useful within biological tissues. However, some care must be taken in the selection of the dye as certain alterations can cause the dye to self-quench, rendering it useless as a singlet oxygen photosensitiser[29]. This self-quenching is especially noticeable in water-soluble phthalocyanine compounds which commonly show high levels of dimerization and aggregation. However, this too can be affected by manipulation of the substituents and axial ligands.

Another feature of these dyes is their tendency to undergo rapid photobleaching. While this feature tends to make them of little use to commercial applications it does make them highly suitable to biological and medicinal applications as this property helps to ensure that the dyes break-down fully after use and do not linger in the system, potentially causes undesirable complications.

2.2.3. Chemical Production of Singlet Oxygen

Photosensitizers are not the only known method of singlet oxygen production, and it has been recorded through a number of different studies that singlet oxygen can be produced as a by-product of the decomposition of a variety of different compound. Many of these compounds could also potentially be linked with the lubrication system of a vehicle engine.

2.2.3.1. Hydrogen Peroxide[30]

The decomposition of hydrogen peroxide has been shown to, under certain circumstances, yield singlet oxygen. Since peroxides are known to be produced within lubricants as they age and begin to deteriorate, hence the addition of peroxide scavengers to lubricant formulations, it is possible that this could be a potential generation point of singlet oxygen without the need for a specific photo-sensitizer.

2.2.3.2. Endoperoxides

One study by Günther et al.[31] focused on the thermal decomposition of 1,4-dimethylnapthalene endoperoxide (DMNE) in acetonitrile at 293K which yielded 25% O_2 ($^1\Delta_g$). The singlet oxygen yielded this way was then reacted with a number of substrates, in most cases yielding similar values for k_R as with singlet oxygen obtained from photosensitization. This study suggested that the thermal decomposition could be a valid method for singlet oxygen production in systems where photosensitization cannot be utilised.

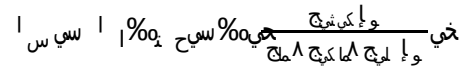
Given that singlet oxygen is known to react with some compounds to form endoperoxides, it is possible that if these were formed within the lubricant it could become a potentially self-catalysed reaction.

2.2.3.3. Other Compounds

The decomposition of other compounds has also been investigated and discussed[30] before but the probability of them being applicable within an engine system is small and therefore will not be discussed here.

2.3. Measuring Singlet Oxygen Production[32]

As stated earlier the proportion of singlet oxygen that is produced in a reaction is noted as the singlet oxygen quantum yield, denoted as Φ_Δ. The singlet oxygen quantum yield of a compound can be calculated using Equation 7



Equation 7

Where;

Φ_T – the quantum yield of triplet formation,

ϕ_{en} – the efficiency of energy transfer,

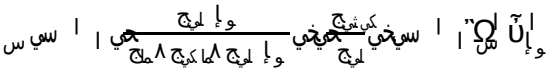
k_{en} – the rate of energy transfer,

k_r – the rate of radiative transitions to the ground state,

k_{nr} – the rate of non-radiative transitions to the ground state,

k_q – the sum of the quenching rate constants for the lowest energy state triplet state of the photosensitizer, $P(T_1)$ by O_2 ($k_q = k_{en} + k_{dO2} + k_{et}$)

One of the major things to consider with these calculations is the other potential pathways that can occur to the excited photosensitizer triplet state, such as radiative and non-radiative decay as well as potential type I reactions which can lead to formation of products other than singlet oxygen whilst still deactivating the sensitizer. As such an alternative method of expressing this is;



Equation 8

Where;

 – is the fraction of the triplet state molecules quenched by O_2 which yield $^1O_2$ or the efficiency of $^1O_2$ formation

$\frac{k_q[O_2]}{k_d + k_q[O_2]}$ is the fraction of the triplet states that are quenched by O_2 overall.

2.3.1. Methods of Measuring $^1O_2$

There are a number of different methods that can be utilised to detect the presence of singlet oxygen all with varying degrees of applicability and sensitivity[33]. These include;

- Fluorescence
- Chemiluminescence
- Electron Spin Resonance (ESR)
- $^1O_2$ trapping
- $^1O_2$ scavengers
- Deuterated water (D_2O)

2.3.1.1. Fluorescence Detection

Fluorescence detection of singlet oxygen involves the use of a fluorescent probe which will show significant changes in the presence of singlet oxygen. The probe will either be made from a compound which by itself is non-fluorescent and, upon either reaction or energy transfer from singlet oxygen, becomes fluorescent, or a compound that is mildly fluorescent and will become highly fluorescent upon reaction or energy transfer from singlet oxygen[34]. This detection method is considered to be one of the most sensitive methods for singlet oxygen detection.

There are a number of different probes that can be used for the fluorescent detection of singlet oxygen the most effective of which are anthracene derivatives. 9,10-Dimethylanthracene (DMA) is an example of this which can be used to detect the generation of singlet oxygen by observing the decrease in the fluorescent signal at 436nm due to the production of the 9,10-endoperoxide from the reaction with singlet oxygen. The advantage of using 9,10-dimethylanthrancene is its high reactivity with singlet oxygen, almost exclusively chemically, as well as its ability to be used in both aqueous and many organic medias.

An alternative method was to combine a well-known singlet oxygen trap, 9,10-diphenylanthracene, which itself does not exhibit fluorescent behaviour, with fluorescein, a fluorophore. The combination of these gave rise to the molecule 9-[2-(3-Carboxy-9,10-diphenyl)anthryl]-6-hydroxy-3H-xanthen-3-one (DPAX) which reacts with singlet oxygen to

form a highly fluorescent endoperoxide product[35]. This probe proved to be highly specified towards singlet oxygen as it showed no change in fluorescent activity when tested with other reactive oxygen species.

This idea was taken one step further by Tanaka et al.[36] who used 9,10-dimethylanthracene as the singlet oxygen trap base over 9,10-diphenylanthracene, to form 9-[2-(3-Carboxy-9,10-dimethyl)anthryl]-6-hydroxy-3H-xanthen-3-one (DMAX). The choice to use 9,10-dimehtylanthracene was down to its higher rate of reaction with singlet oxygen, 9.1×10^8 $mol^{-1}s^{-1}$ vs 1.0×10^6 $mol^{-1}s^{-1}$, which lead to DMAX having a higher sensitivity than DPAX.

The endoperoxide product of reaction for DMAX showed to have a fluorescence quantum yield approximately 1.5 times higher than that of the DPAX endoperoxide, making it easier to detect. The last major advantage was that the concentration of the DMAX product was shown to be in a linear relationship with the rate of singlet oxygen production, which allows this probe to potentially be used to quantitative measurements of singlet oxygen. As with DPAX, DMAX also showed specificity towards singlet oxygen after being tested with other reactive oxygen species and showing no change in fluorescence.

2.3.1.2. Chemiluminescence Detection

Like fluorescence detection, chemiluminescence detection also uses probes which are affected by the presence of singlet oxygen. These probes are often an improvement over fluorescent probes as they can improve the signal-to noise ratio by reducing or eliminating background fluorescence and various sources of light scattering. It can also be noted that these probes often only need to be used in low concentrations due to their high sensitivity, which helps to decreases the likelihood of results being effected by secondary reactions with the probe. However, there are some drawbacks in that not all chemiluminescent probes are specific to singlet oxygen detection and as such can give false results if there are other reactive oxygen species present. An example of this is Cypridina luciferin analogs which are known to be highly sensitive chemiluminescent probes for singlet oxygen but are also known to detect O_2^-.

There are two types of chemiluminescence that can arise from singlet oxygen, monomol light emission and dimol light emission[33]. Dimol light emission arises from the deactivation of two singlet oxygen molecules simultaneously and results in two emissions within the red region of the visible spectra at 634 and 703nm[37]. The monomol emission of singlet oxygen is responsible for the emission seen in the near-infrared region at 1270nm. Direct measurement of this

emission is the most popular method of measuring singlet oxygen as it can be used to determine multiple properties and is a non-invasive method. Since 2000 singlet oxygen luminescence detection has been considered the standard for measuring and determining singlet oxygen formation yields, lifetime and quenching constants.

Until recently the most commonly used detectors for singlet oxygen luminescence detection were cryogenic germanium diodes, like the one used for measurements during this project. However, while these detectors are effective they do require cooling with liquid nitrogen prior to use, which can become time-consuming, and become far less sensitive the longer they are used as the detector warms, unless time is taken to cool it again. Recently the introduction of near-infrared photomultiplier tubes has helped eliminate many of the issues found with germanium diodes as they show sensitivity an order of magnitude higher and do not require cryogenic cooling.

2.3.1.3. Electron Spin Resonance (ESR) or Electron Paramagnetic Resonance (EPR)[38]

Electron spin resonance is a method that allows for direct detection and measurement of the unpaired spins of free radicals. It is one of the preferred methods of free radical reactive oxygen species such as the superoxide and hydroxyl radicals; although this method has also been applied to singlet oxygen. The main issue with electron spin resonance is the specificity and expensive nature of the equipment required. Electron spin resonance can also suffer from low sensitivity under certain conditions, especially in aqueous solutions and at room temperature.

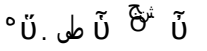
However, there are methods to increase the sensitivity of electron spin resonance, namely by the use of non-paramagnetic spin traps. These spin traps react with the radicals to form semi-stable paramagnetic compounds which build up in solution to the point where they reach detectable levels.

One spin trap which is used in a number of studies for the detection of singlet oxygen is 2,2,6,6-tetramethylpiperidine which reacts to give the detectable product 2,2,6,6-tetramethylpiperidineoxyl (Deepak et al. Michalaska et al.). A study by Sang *et al.* found that the spin trap 5,5-dimethylpyrroline N-oxide, normally used to detect hydroxyl radicals, reacted with singlet oxygen as well. However, this is also a drawback of this spin trap, since it does not exclusively react with singlet oxygen.

2.4. Quenching of Singlet Oxygen

Quenching is the process by which the lifetime of an excited state is shortened due to the effect of an outside source; this can either be via reaction or energy transfer to the solvent or another compound within the system, often one added specifically to be involved in a quenching reaction.

As stated there are two possible method by which an excited state can be quenched; a reaction or energy transfer. If a chemical reaction occurs, resulting in the formation of a new product, then the process is termed as chemical quenching and the rate at which this quenching reaction occurs in given as k_c.



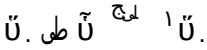
Equation 9

Where;

Q – Quencher,

P – Products

If an energy transfer reaction occurs, resulting in no product formation, then the process is termed as physical quenching and the rate at which this quenching reaction occurs is given as k_p.



Equation 10

However, the quenching of an excited state may not be exclusively via one pathway, but instead can occur via both pathways at the same time. Therefore, the overall rate of quenching of an excited state, k_Q, can be expressed as;

Equation 11

The process of quenching will be discussed in further detail in chapter 4.

2.5. Solvent Effects

Fernandez *et al*.[26] conducted experiments into singlet oxygen generation by a variety of sensitizers, this time in a pH 7.4 phosphate buffer containing 1% Triton X-100. The samples

were irradiated using a xenon arc lamp and the photosensitization of lysozyme was used as an internal actinometer. The values obtained in this study were congruent with others obtained under similar conditions but involving different measurement techniques. An example is the singlet oxygen quantum yield value obtained for mesotetra-(4-sulfonato-phenyl)porphine, سي س πϕ ,ρin a study by Spikes[39] where an O_2 uptake measurement technique was used.

Research by Abdel-Shafi and Worrall[40] looked into the use of supercritical fluids as a possible solvent for singlet oxygen production. One of their studies focused on singlet oxygen production and its decay in supercritical xenon. This study found that the solvent mediated deactivation played a crucial role in determining the singlet oxygen lifetimes observed. It was also found that as the pressure increased the rate that singlet oxygen was quenched by ground state oxygen, ῀Ωꭓ, also increased. In a separate study it was shown that there was very little temperature dependence for the singlet oxygen decay constants measured between 295-325K[41].

Previous work by Schmidt[42] analysed data from a number of studies into the effect of solvent polarity on the pathways in which singlet oxygen is produced by dye sensitization. These potential pathways are either via a charge-transfer reaction or a non-charge transfer reaction. The primary pathway for formation was *via* the non-charge transfer pathway and involved the formation of an encounter complex between the excited triplet sensitizer and the ground state oxygen which then underwent internal conversion before dissociating to give the ground state sensitizer and either $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$ or $O_2(^3\Sigma_g^-)$.

It was noted that if charge transfer interaction were prevalent with the sample then exciplexes of the excited sensitizer triplet and the ground state triplet oxygen would form in competition with the internal conversion of the encounter complexes seen with the non-charge transfer pathway.

Through their investigation, Schmidt found that only these charge transfer interactions were affected by the polarity of the solvent used. This was due to the fact that the rate constants for the formation of the exciplexes was dependant on the change in free energy of the exciplex formation, ΔG_{CT}. In turn ΔG_{CT} can vary depending on the sensitizer's triplet energy, oxidation potential and the polarity of the solvent.

2.6. Singlet Oxygen Reactions

As with many other oxidative reactions, oxidation via singlet oxygen can often be seen as detrimental or harmful, especially when considered within a biological medium when singlet oxygen reactions can cause rapid cell death[13]. However, this is not always the case. While it is true that singlet oxygen reactions can be detrimental to biological systems it is also possible to harness this in a way that is beneficial, such is the case with photodynamic treatments for cancer where singlet oxygen production is localised to specifically target cancerous cells, destroying them with minimal harm to any surrounding healthy cells.

Another example is the use of singlet oxygen in the production of juglone (5-hyroxy-1,4-naphthalenedione), a chemical that has multiple uses from a herbicide to a food colouring. Singlet oxygen can be used to produce juglone by via oxidation of 1,5-dihydroxynapthalene. Juglone itself can be quite expensive to buy directly, approximately £105 for 5 grams, whereas 1,5-dihydroxynapthalene is nearly a fifth of the price, meaning that production via singlet oxygen oxidation is a far more cost effective option.

However, the most important reaction of singlet oxygen for this project is the –ene reaction of singlet oxygen. This reaction of singlet oxygen was first discovered in 1953 by Günther Schenck[43].

2.7. Other Reactive Oxygen Species

Due to the conditions found within a car engine, specifically within the engine oil system, it is feasible that singlet oxygen may not be the only reactive oxygen species that is produced. It is important to consider these other possible species as they may be involved in reactions which compete with the quenching of singlet oxygen and thus could affect the applicability of some singlet oxygen quenchers.

Reactive oxygen species are oxygen containing molecules or compounds that show a higher reactivity than molecular oxygen. These can include a variety of things including; molecules such as hydrogen peroxide (H_2O_2), ions such as the hypochlorite ion (ClO^-) and peroxy-nitrate ($ONOO^-$), radicals such as the hydroxyl radical ($^{\cdot}OH$) and the superoxide radical ($^{\cdot}O_2^-$) which can be classed as both an ion and a free radical[44,45].

2.7.1. Hydrogen Peroxide (H_2O_2)

Although hydrogen peroxide is not a radical, nor does it have any unpaired electrons, its high reactivity places it as a reactive oxygen species along with the others. Hydrogen peroxide has the ability to act as both a strong oxidant and reducing agent and can often be found to play a significant role in the formation of other reactive oxygen species, especially the hydroxyl radical which will be discussed later.

While there are a number of different methods for detecting hydrogen peroxide often optical detection methods are preferred, especially at low concentrations of hydrogen peroxide. These methods include; fluorescence, absorbance and chemiluminescence. Of these fluorescence and absorbance involve more complex requirements for measurements, such as a stabilised excitation or photon source, than chemiluminescence which can use reagents such as luminol and peroxyoxalate[33].

2.7.2. Peroxynitrite ($ONOO^-$)

Peroxynitrite is a short-lived reactive oxygen species which can be formed via a few different methods, the simplest of which involves the deprotonation of peroxynitrous acid (ONOOH). It is also possible to form peroxynitrite from the precursors $^{\cdot}NO$ and $O_2^{-\cdot}$ or via reaction between acidified hydrogen peroxide and nitrate. However, peroxynitrite formed via this reaction will readily thermally decompose and has to be stored at -80^{o}C as soon as possible after formation to prevent this, making it highly unlikely to occur within an engine block. Its decomposition can harbour its own problems in the other reactive oxygen species that can be formed from this, namely the superoxide radical.

An interesting occurrence that was found when exploring chemiluminescent detection of peroxynitrite was an observed peak around the known wavelength for singlet oxygen chemiluminescence at 1270nm[46]. Others have disputed this and attributed this signal to interference from residual hydrogen peroxide left over from the initial formation reaction[47,48] and that singlet oxygen was not formed via a peroxynitrite reaction. This was also concluded by Pollet *et al*[49] who suggested the chemiluminescence was due to other excited species produced by side reactions within the testing medium.

Overall peroxynitrite is a difficult reactive oxygen species to detect, due to its short lifetime and difficulties in isolating the molecule or being able to detect it directly. The need to separate

any signals that could be produced by peroxynitrite from its precursor molecules also makes detection problematic.

2.7.3. Hydroxyl Radical (·OH)

The hydroxyl radical is the most reactive of the oxygen containing radicals, with a half-life of approximately 10^{-9}s[50]. It readily reacts with many molecules, both organic and inorganic, which would be highly problematic within an engine oil. Its presence is combatted within the engine oil by the use of radical scavengers, like the sulfurized olefin studied within this project, which can deactivate the radical *in situ*.

The hydroxyl radical could be formed within an engine oil via a few different methods, although the main ones involve the reaction of hydrogen peroxide leading to the formation of the hydroxyl radical as a product. If metal impurities are present within the oil, which is likely to occur over time if the oil is not drained and replaced, then it is possible for hydrogen peroxide to react with these, especially ferrous ion impurities, *via* a Fenton reaction to produce hydroxyl radicals[33].

ü ر طى″O. ŭ. º ü ر٨º طى ⁸ŭ ″Oطى ŭ ″Ó Equation 12

It is also possible for hydrogen peroxide to react with an oxygen ion to form the hydroxyl radical *via* a Haber-Weiss reaction.

″O. ŭ. طى ŭ.٩ º ŭ. طى ŭ ″Ó طى ⁸ŭ ″O Equation 13

The hydroxyl radical itself can be hard to detect or measure directly and as such detection relies heavily on its reactivity with other molecules which can be measured more readily. The most effective method for this is electron spin resonance (ESR); however, the equipment and reagents for this method are expensive so it is not always ideal[50].

An alternative method is the use of luminescent compounds, such as luminol and lucigenin. The hydroxyl radical will readily react with the ferrous ion in luminol, resulting in luminescence of the luminol molecule which can then be measured[51,52]. However, it is possible for other reactive oxygen species to be produced as well, especially the oxygen ion and hydrogen peroxide, which can affect results and makes it hard to isolate the luminescence resulting from the hydroxyl radical. Lucigenin on the other hand reacts with oxygen ions,

singlet oxygen and hydrogen peroxide, and so could be used in conjunction to isolate the results due to the radical.

2.7.4. Superoxide Radical ($\cdot O_2^-$)

The superoxide radical is one of the less-reactive reactive oxygen species addressed here and is formed by the donation of an electron to oxygen. It is considered to be a weak base and does not appear to be a strong oxidant at neutral PH; however, it is possible for the superoxide radical to be a one-electron reductant of metals. It has also been noted that the superoxide radical is very soluble in water, which lessens the likelihood of this particular reactive oxygen species occurring within an engine oil. While it may not be very reactive itself, the superoxide radical is able to react to produce other species such as hydrogen peroxide and peroxynitrite which are far more reactive oxygen species.

The superoxide radical itself has a relatively short half-life, which can make it difficult to measure and detect; however, chemiluminescence has been shown to be a fairly reliable method of detection whilst offering high sensitivity. The main reagents used for chemiluminescent detection of the superoxide radical are luminol and lucigenin, the latter of which has shown to be sensitive enough to detect low concentrations of the superoxide radical[53–55]. However, neither of these reagents are selective towards the superoxide radical in their detection which can cause problems if there is potential for other reactive oxygen species in a system.

2.7.5. Production of Reactive Oxygen Species

Since the engine oils are utilised in a metal rich environment there is a very high likelihood of metal particles existing within the oil. This comes with its own complications for the oil, however, with a specific focus on reactive oxygen species it has been shown that transition metals especially can catalyse the production of reactive oxygen species [56,57]. See *et al.*[45] looked into the relationship between the concentration of transition metals and the presence of reactive oxygen species in combustion aerosols. One of the types of emission particles that were investigated were those produced by on-road vehicles. They found that a number of water-soluble transition metals showed a correlation with the concentration of reactive oxygen species present in their samples.

Another source of possible catalysis that has been found is the particles, especially nano-soot particles, produced as a by-product of combustion within the engine. While the oil system of the motor is mostly separated from the combustion chamber, it is still possible for particulates to find their way into the oil and as such increase the chance of reactive oxygen species production. Chuang *et al.*[58] performed a study into the formation of reactive oxygen species driven via the production of soot produced through the burning of incense, diesel and carbon black. In this study they found that there was a relationship between the physiochemistry of the particulate matter produced *via* combustion as well as a correlation between the production of nano-soot particles and reactive oxygen species production.

3. Engine Oils

3.1. Lubricants[59–61]

Lubrication is a vital part of the automotive industry as it helps to extend the working lifetime of moving parts by forming a protective layer over exposed parts, reducing the wear and damage that can occur during use.

3.1.1. Base Stocks

Most non-synthetic lubricant base stocks are comprised of a combination of compounds extracted from crude oil. There are two types of base oils that can be used for lubricants; these are conventional and unconventional base oils. A base oil stock is deemed conventional or unconventional due to the refinement method used. These base oils make up anywhere from 70 – 98% of the overall lubricant, the remainder is made up of additives. Since the base stock is what provides the actual lubrication, these additives are used to help prolong the working lifetime of the base stock.

Some of the properties required for a good quality base stock include; suitable viscosity, ability to dissolve additives and/or contaminants, foam resistance and oxidation stability. Oxidation stability is the main point of interest in this project as many different anti-oxidant additives that are commonly used in conjunction with base stocks will be tested, as well as some other potentially useful naturally occurring antioxidants.

A study by Mascolo *et al*.[62] studied the thermal degradation of three commercially available synthetic industrial lubricants. Two of these lubricants were of triaryl phosphate compositions while the other was a fatty acid composed of methyl and ethyl esters. The lubricants were tested between temperatures of 400-1000^{o}C and it was found that for both types of base stocks the main by-products of thermal degradation were aromatic hydrocarbons, mostly comprised of benzene and polycyclic aromatic hydrocarbons, with by-product formation peaking between 700-800^{o}C.

The main issue faced from thermal degradation by-products is that they tend to be more readily oxidised and polymerised. Polymerisation especially can lead to significant changes in the overall viscosity of the lubricant as well as the formation of deposits within the engine system.[63]

3.2. Lubricant Additives

3.2.1. Pour Point Depressants

Automotive engine oils operate in the liquid phase to provide lubrication. Therefore, it is imperative to maintain the oil's ability to flow through the system, even at low temperatures, e.g. engine start up on a cold day. The primary function of pour point depressants is to reduce the temperature at which waxy crystal structures will form within the oil. This aids the ease of flow of the oil at low temperatures. Pour point depressants tend to be polymers with a high molecular weight, of which there are two general types. Alkylaromatic polymers will inhibit growth and adhesion of wax crystals to each other by instead adhering to the crystals as they start to form. The other type of pour point depressants are polymethacrylates which will inhibit crystal growth by co-crystallising with them. On average the pour point temperature will be reduced by 11-17^{o}C, although depending on the type of base stock used it can be possible to drop the pour point by up to 28^{o}C[61]

3.2.2. Viscosity Index Improvers

Viscosity index improvers are long-chain, high molecular weight polymers which change physical configuration at certain temperatures to affect the viscosity of the lubricant. The function of these polymers is to increase the relative viscosity of the oil at high temperatures rather than at low temperatures. This allows the oil to flow freely through the system but still have sufficient viscosity to provide effective lubrication.

The types of polymers that are used for this function include; acrylate and methacrylate polymers, olefin polymers and copolymers, and styrene butadiene copolymers. Viscosity index improvers work in conjunction with pour point depressants to help keep the lubricant at a suitable viscosity at the widest temperature range possible.

3.2.3. Defoamants

Foaming of engine lubricants is highly unfavourable so defoamants are used to combat this issue. The requirement of defoamants for lubricant oils is dependent on the type of base stock used, its viscosity and the method/degree of refinement it underwent. Defoamants are generally thought to work by attaching to air bubbles within the oil and forming larger air bubbles by combining smaller ones. These larger air bubbles will then rise to the surface of the oil more readily than the smaller bubbles and then collapse, releasing the air.

The most commonly used defoamants are silicone polymers. However, there is an issue regarding the use of these as they tend to be insoluble in oil and so need to be carefully selected for certain polymer size to avoid settling during long periods of storage. The procedure for blending the polymer can also help to combat this issue. A secondary issue with the use of silicone polymers is that they can increase air entrainment within the oil itself. The use of organic polymers in place of silicone polymers has been suggested as a solution to these problems; however, the organic polymers are required in much higher concentrations that the silicone polymers in most cases.

3.2.4. Rust and Corrosion Inhibitors

Corrosion inhibitors work by adhering or chemically boding to the metal within the system to form a protective film across exposed surfaces, preventing potentially corrosive compounds from being able to access, and thereby attack, the metal surface. These corrosive compounds will often be by-products formed during combustion such as; organic acids produced from the combustion of sulphur. To combat these products highly alkaline compounds are often used, some of which can also act as detergents (See Detergents and Dispersants).

Rust inhibitors work in a very similar way to corrosion inhibitors in that they will form a protective layer over exposed surfaces. However, rust inhibitors are used to protect against water penetration. These compounds will often be amine succinates or alkaline earth metal sulfonates and are found in almost all lubricant oils. The primary issue with the use of rust and corrosion inhibitors is that due to their having to react or adsorb to the exposed surfaces their concentration within the oil can become depleted over time, therefore requiring replacement of the oil.

3.2.5. Anti-wear Additives

Anti-wear additives help to reduce friction, wear and general scuffing or scoring around moving parts within the engine. Since the primary function of a lubricant is to reduce friction these additives are very useful. It is important to try and reduce friction due to the increase in temperature it can cause, which can lead to welding and the shearing of parts, as well as reducing the overall probability of shearing or scoring from occurring as this can introduce metal particulates into the oil.

There are two general types of anti-wear additives. Which additives and what concentrations are used will vary according to the requirements of the lubricant. Mild anti-wear additives, also

known as friction-reducing or boundary lubrication additives tend to be long chain polar compounds, such as fatty acids, oils or esters, which adsorb to metal surfaces during contact to form a layer between contacting surfaces. The second type of anti-wear additive is discussed below.

3.2.6. Extreme Pressure Additives

Higher temperatures and heavier loads produce added pressures of contacting surfaces, including increased sliding. In these conditions, extreme pressure additives are required to help reduce friction, wear and damage to the contacting surfaces. Extreme pressure additives will chemically react with contacting metal surfaces to produce a protective film which is insoluble in the base stock oil. This reaction will occur faster at higher temperatures which occur under these more extreme conditions.

These additives tend to be sulphur, chlorine or phosphorus containing compounds, either alone or in conjunction with each other. Which of these may be used will depend on the requirements of the system the lubricant will be used in.

3.2.7. Detergents and Dispersants

These types of additives are highly important in maintaining a lubricant's functionality and help to improve the lubricant's overall performance[64,65]. Detergents and dispersants help to prevent/reduce the formation and accumulation of potentially harmful deposits within the oil which can lead to increased wear, reduced circulation, sticking of parts and thus cause issues with the functioning of crucial components within the engine. Once these deposits have formed within the engine it is almost impossible to remove them without mechanical cleaning which is both time consuming and expensive. There is however an issue with the use of detergents and dispersants in that they do not remove the contaminants from the oil, instead they keep them dissolved in the oil so that they do not form deposits. This means that regular draining and replacement of the oil and oil filter is required to actually remove the contaminants.

Detergents primarily function at high temperatures by chemically neutralising precursors to deposit formation, whereas dispersants work at lower temperatures by suspending potential sludge or varnish forming materials, preventing them from reacting together. Although these two types of additive have differing functionalities they are not mutually exclusive but rather it is possible for some compounds to have properties suitable to both types.

There has been a lot of research into more effective and efficient dispersants and detergents and a number of different compounds groups have been identified as potentially useful. However, the primary types of compound used for detergents are organic soap or salts which incorporate alkaline earth metals. A number of calcium and magnesium containing compound have been identified as good detergents and dispersants including; calcium/magnesium containing sulfonates, calcium phenates and phenol sulfides are among the most widely used additives. These compounds can either be neutral compounds or overbased (discussed later).

These types of organo-metallic detergents have some issues associated with them as they tend to leave behind ashy residues if they are combusted which can potentially be detrimental to the engine and itself contribute towards deposit formation. However, in some circumstances this ashy residue can coat exposed surfaces between connecting parts and provide added anti-wear properties.

Types of dispersant that can be used are polymeric dispersants and ash-less dispersants. Compounds within this category tend to be long-chain hydrocarbons which have been acidified and then neutralised so that they contain a basic nitrogen containing group. The hydrocarbon chain provides stability to the dispersants within the base oil, while the basic nitrogen group gives the dispersant an active site at which it can suspend unwanted contaminants.

Overbased detergents work by neutralising acidic by-products as they form. It has been suggested that after the base has been released by the detergent the remaining surfactant molecule can also act as a detergent, improving the functionality of overbased detergents further[66]. Overbased detergents can include; alkyl sulfonates, sulfurised alkyl phenates, salicylates and calixarates[67].

3.2.8. Antioxidants

One major issue that needs to be addressed within the field of lubrication is that when the lubricant is heated and oxygen is present in the system oxidation will occur. The result of oxidation will be the deterioration of the base stock, making the lubricant less effective. If oxidation continues to occur, by-product concentrations can increase, including corrosive compounds such as organic acids, and plaques or varnishes can start to form on the metal surfaces that are exposed within the engine. It has been shown that the presence of transition metals, such as copper or iron, can catalyse the oxidation reaction via the production of reactive

oxygen species[45,56,57]. The oxidation process is considered to proceed via a free radical process; the proposed processes are shown in figure 6[68].

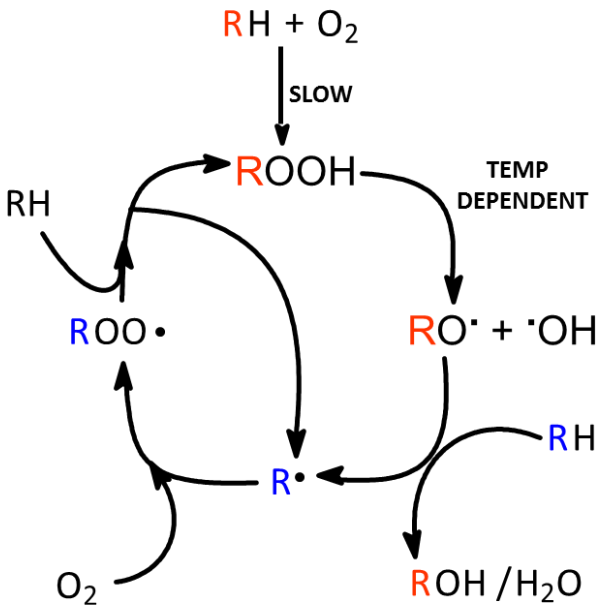


Figure 9 - Proposed Mechanism for Lubricant Oxidation[68]

There are two general types of antioxidants the first type will inhibit the oxidation process by reacting with initiator compounds, peroxy radicals and hydroperoxides to form inactive compounds. The second type of antioxidant inhibits oxidation by decomposing reactive materials into less reactive compounds.

At temperatures below around 370K this process proceeds slowly, at this point in the process the first type of anti-oxidants are most effective. Examples of these anti-oxidants include hindered phenols and aromatic amines; a sample of each type has been provided by Lubrizol for testing (figure 10 & 11).

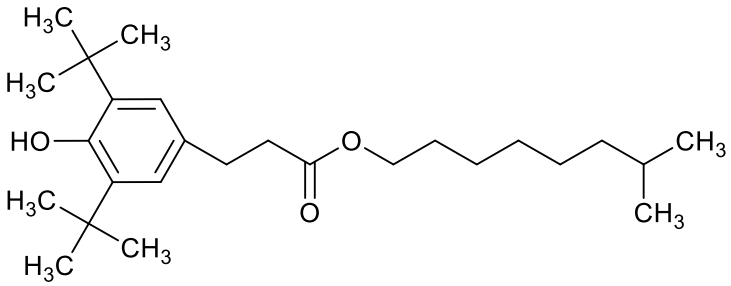


Figure 10 - Lubrizol Phenolic Antioxidant

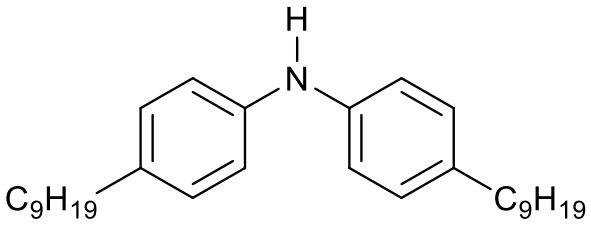


Figure 11 - Lubrizol Aminic Antioxidant

At temperatures above around 370K the previously mentioned catalytic effect of metal particles becomes a more prominent factor in the oxidation process as they begin to catalyse the reaction more. Therefore, anti-oxidants that work to reduce or prevent this catalytic effect are required. Most compounds in this category are known as metal deactivators as they work by forming a protective layer over the metals effectively blocking anything from being able to access the metal surface. An example of this type of additive is the dithiophosphates, in particular zinc dithiophosphate which is also able to decompose hydrogen peroxide at temperatures above 370K.

It should also be pointed out that other additives will contribute to a reduction in oxidation by performing their roles. For example, detergents by reducing the concentration of organic acids in the oil they can help to reduce the rate of oxidation. Therefore, it is important to carefully balance the additives required in a lubricant to help promote synergies and increase the overall effectiveness of the lubricant over its working lifetime.

4. Antioxidants and Singlet Oxygen Quenchers

4.1. The Quenching of Singlet Oxygen

Quenching is the process by which the lifetime of an excited stated is shortened and can occur via two differing processes. The first process is known as physical quenching, whereby the energy from the excited state is transferred away to another molecule with no chemical change to either compound. This is most often observed as the quenching occurring between an excited state and the solvent it is dissolved in.

The other process is known as chemical quenching and involves the energy from the excited state begin transferred or redistributed away via a chemical reaction with another compound, resulting in the formation of a new reaction product. This type of process will be capitalised on in this project as a method of observing singlet oxygen production and other quenching occurring by using a compound known to be exclusively a chemical quencher of singlet oxygen and observing any changes in the reaction rate when other quenchers are present in the solution. This quencher will be known as the sacrificial acceptor throughout the project.

Equation 14 and 15 give a basic description of the two quenching processes and the resulting products.

Equation 14

Equation 15

Where;

ö – Anti-oxidant

– Rate constant for physical quenching

– Rate constant for chemical quenching

- Product

For the singlet oxygen quenchers that were explored throughout this research it is hoped that the primary process for quenching used would be physical quenching, due to the absence of product formation and the potential for the quencher to disperse the quenched energy and be able to react with singlet oxygen again, thereby making it a more effective quencher over a longer period of time.

Quenching is a process in photochemistry whereby the lifetime of an excited state is shortened. This can cause the quantum yield of a reaction to decrease, or it can be a desired process during a reaction, such as energy or electron transfer[4]. This project looked into the quenching ability of a number of antioxidants with regards to singlet oxygen by looking at the difference in the concentration of a sacrificial acceptor molecule with and without the antioxidant present. The addition of the antioxidant opens another pathway for the singlet oxygen. This could be either a physical pathway (Equation 14), whereby there is no overall change in the chemistry of the compounds, or a chemical pathway (Equation 15), where the antioxidant reacts with the singlet oxygen to form a product.

Part of this project will look into the separation of the constants for these two types for quenching from the overall quenching constant. Ideally, physical quenching will be the primary pathway for the antioxidants tested as this will lead to them being present in the system for longer whilst still quenching.

Several singlet oxygen quenchers were investigated throughout this project. Some were well known, naturally occurring, quenchers which had been previously investigated for their singlet oxygen quenching capacity, while the remaining were synthesized for use within engine oils as either radical scavengers or peroxide inhibitors.

The primary objective was to investigate the effectiveness of the engine oil antioxidants compared to the naturally occurring antioxidants in different mediums. However, potential synergies or inhibition between the various quenchers was also investigated to see if certain combinations would provide stronger quenching than that provided by the individual quenchers.

4.2. Vitamin E

The group of molecules classed as vitamin E can be subdivided into two groups; the tocopherols, of which there are four known; α, β, g and d, and the tocotrienols, of which there are also four known; α, β, g and d. The tocopherols have a saturated side chain at the 2- position

of the chromanol ring, called a phytyl side chain, while tocotrienols have a side chain with three double bonds at the 3', 7' and 11' positions[69].

The antioxidant α-tocopherol, figure 12[70], was used within this study as it is well documented as a strong antioxidant and singlet oxygen quencher.

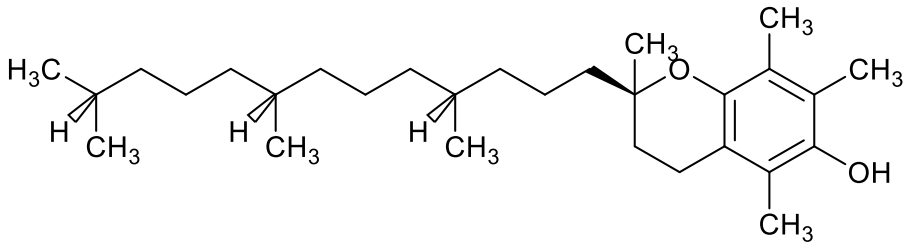


Figure 12 - Chemical Structure of Alpha-tocopherol[70]

These compounds function as antioxidants be scavenging peroxyl radicals, thus preventing propagation of free radical reactions[71,72]. The structures of the molecules support the theory that antioxidant efficiency increases with the ability of the molecule to donate protons[72]. Many studies have investigated into the antioxidant efficiency of vitamin E[73,74,75], mostly in the form of α-tocopherol.

Out of all the vitamin E compounds, α-tocopherol is the most abundant in nature[76], and shows the highest antioxidant activity.[77] This high level of antioxidant activity has been suggested as being due to the increased efficiency of hydrogen donation as ring methyl substitution occurs. It has also been previously investigated for its singlet oxygen quenching[32] allowing for comparison of results with this projects' finding to ascertain the accuracy and reliability of any findings.

All of the compounds within the Vitamin E group are known lipid-soluble antioxidants[76] making them of strong interest for this project due to the similar properties between lipids and oils. Kim and Paik conducted a study into the effect of the four tocotrienols on the singlet oxygen oxidation of lard[78] .

In their experiments the rate of oxidation of various concentrations of lard, in methylene chloride, was determined both with and without the antioxidants present. Singlet oxygen was produced by exciting chlorophyll, which was added to the solutions as a sensitizer, over a four-hour period. Overall, they found that while all four tocotrienols showed quenching of singlet oxygen it was α-tocotrienol that showed the most significant reduction in oxidation rate

For tocopherols, in polar solvents, physical quenching of singlet oxygen predominates over chemical quenching[79]. The order of efficiency for the tocopherols is α > β > g > d[80,81]. However, it has been shown that over prolonged periods g- and d- tocopherol may be more effective since they have a higher stability to photosensitized oxidation than α- and β- tocopherol[82]. The efficiency of singlet oxygen quenching by the tocopherols appears to be dependent on the free phenolic hydrogen since when Kaiser et al.[80] tested similar molecules with an ether or ester bond the quenching activity was almost nil.

The effect of temperature on the singlet oxygen quenching efficiency of tocopherols has also been investigated and was shown to have an interesting effect. It has been shown that temperature can play an effect on the efficiency order of the four tocopherols. The order of efficiency at low-mid temperatures is the order stated early in this review, while at high temperatures the order of efficiency is reversed, d > g > β > α[81].

Research by Trebst *et al*[83] looked into the role of tocopherol, primarily α-tocopherol, as a singlet oxygen quencher within photosystem II of *Chlamydomonas reinhardtii*. From their experiments they found that the plants produced higher levels of α-tocopherol as the intensity of the light they absorbed increased. This correlated with an increase of singlet oxygen being produced within the cell. They go on to state that the more tocopherol is needed to be produced as the process of quenching singlet oxygen primarily follows the chemical pathway and as such the tocopherol is oxidized and consumed, therefore being unable to continue quenching.

The reaction between the tocopherol and singlet oxygen involves addition of the oxygen on the 8 position of the tocopherol, forming 8-hydroperoxychromanone.[84] The reaction may be reversible unless the molecule is then hydrolysed, forming a tocopherolquinone, which may occur under mildly acidic conditions. This could cause problems within an engine system due to the high chance of mildly acidic conditions caused by other reactions within the engine oil.

4.3. Squalene

Squalene, more commonly known as shark liver oil, is a triterpene compound containing six double bonds, see figure 13[85]. It is a compound widely found in nature, primarily within the livers of sharks hence its common name, but is also found within various grain and vegetable oils[86] as well as, as a biological intermediate in many plants and animals, including humans where it is known to be one of the major lipids found on the skin[87]. As such it has been studied

previously for its antioxidant and singlet oxygen quenching properties, with a primary focus on biological systems[88].

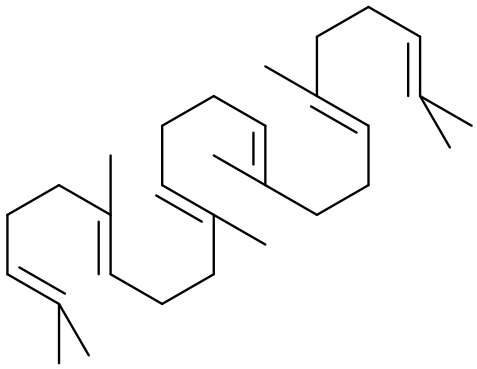


Figure 13 - Chemical Structure of Squalene[85]

Kohno *et al*.[89] investigated the kinetics of singlet oxygen quenching by squalene, along with α–tocopherol and various lipids similar to those found on human skin, in n-butanol. They found that while the quenching constant for squalene was less than that of α–tocopherol it was significantly higher than those from other lipids found on the skin surface.

Within their work, Kohno *et al*. observed that the structure of squalene contains six 2-methyl-2-pentene units and, when comparing the k_Q values for the two, found that the k_Q for squalene was approximately six times larger than that of 2-methyl-2-pentene. They went on to suggest that the singlet oxygen quenching activity shown by squalene originates from the presence of the 2-methyl-2-pentene units in its structure.

Furthermore, they found that the value of k_Q was greatly reduced when replacing one methyl group in 2-methyl-2-pentene with hydrogen, suggesting that the electron donating properties of the methyl group may play a significant role in the efficiency of singlet oxygen quenching. These methyl groups are also shown to lower the ionisation potential of the compound, leading to a very low ionisation potential for squalene. It was also noted that the methyl groups within squalene are able to provide hydrogens for an ene reaction[88], which may provide a chemical quenching pathway for singlet oxygen. They went on to conclude that the small ionisation potential of squalene, coupled with the methyl groups being able to provide hydrogens for the ene reaction, lead to its heightened capacity for singlet oxygen quenching over other skin surface lipids.

Dessi *et al.*[90] looked into the protective effect of squalene against the oxidation of various polyunsaturated fatty acids. This study focuses on temperature-dependent autoxidation as well as UVA mediated oxidation, mimicking singlet oxygen dependent reactions. The results of the study showed significant inhibition of the oxidation process, ranging from 22-50%, for the polyunsaturated fatty acids tested when squalene was added at a 7:1 (polyunsaturated fatty acid: squalene) molar ratio.

They suggested that squalenes higher resistance to peroxyl radical attack over the other polyunsaturated fatty acids, shown in the study by Kohno *et al.*[89], was an important factor in its ability to act as a protective agent; since it is unable to propagate the chain reaction of lipid peroxidation.

4.4. Lubrizol Aminic

The first of the three antioxidants provided by Lubrizol that were investigated throughout this project is an amine based antioxidant (Figure 14). This is known to be an effective antioxidant and is frequently used in Lubrizol engine oil formulations.

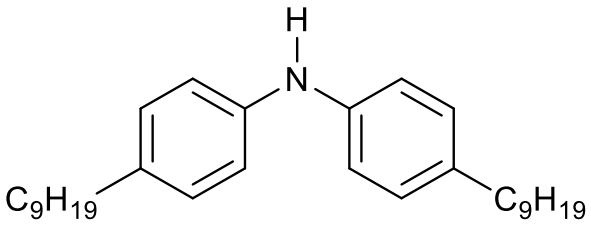


Figure 14 - Primary Chemical Structure of Lubrizol Aminic Antioxidant

Due to the nature of its synthesis, this antioxidant is not fully purified and as such samples are likely to contain some traces of synthesis by-products. A breakdown of the potential products of the synthesis and their approximate percentages within the mixture is show in table 3. Purification was not performed on the sample, since that is how the sample would be found in a formulation and therefore was of the highest interest to see how it performed in its current state.

Table 3 - Breakdown of Aminic Antioxidant Composition

Unreacted diphenylamine	0.7%
Monoalkylated on phenyl	21.9%
Monoalkylated on nitrogen (assumed)	2.4%
Dialkylated on phenyl	64%
Dialkylated with one alkyl on nitrogen (assumed)	7.4%
Trialkylated total	3.5%

To allow for the calculation of concentrations of solutions containing the aminic antioxidant it was assumed that all of the product present was the dialkylated version. As such the RMM value was calculated as 421.7 $gmol^{-1}$.

Given the structure of this antioxidant it would be expected for singlet oxygen to react at the amine group in the center, delocalizing the energy across either/or both of the two rings. While this specific antioxidant has not been tested for its ability to quench singlet oxygen previously, there have been several studies into the effectiveness of quenching for many nitrogen-containing compounds that could be considered similar enough in structure or properties for comparison.

Ballardini *et al*[91] investigated the singlet oxygen quenching of various nitrogen containing compounds, including hindered amine light stabalisers (HALS). They discuss a suggested mechanism for how these compounds stabilize by preventing oxidization via the formation of a stable nitroxyl radical which can react with other radicals within a system to form a hydroxylamine. This mechanism is a self-catalysing system as the final hydroxylamine is able to further react to reform the stable nitroxyl radical as so on.

If this is the same mechanism by which the aminic antioxidant functions, then it would suggest that the aminic antioxidant should show significant singlet oxygen quenching.

4.5. Lubrizol Phenolic

The second antioxidant compound provided by Lubrizol is a phenol based compound, figure 15.

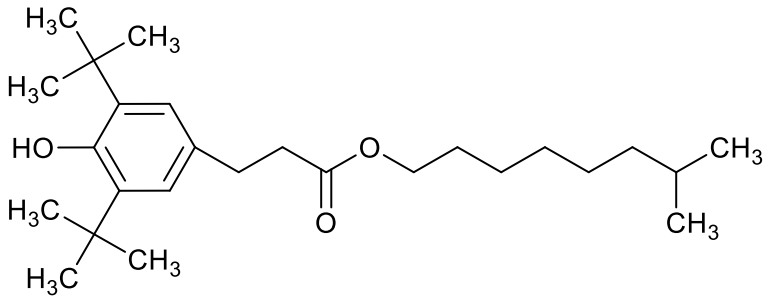


Figure 15 - Primary Chemical Structure of Lubrizol Phenolic

The compound features two branching hydrocarbon groups off the phenol ring as well as an ester group within the hydrocarbon tail. This antioxidant is somewhat similar in structure to α-tocopherol and as such is expected to show at least moderate singlet oxygen quenching. However, the t-butyl groups on the phenol could potentially lower the efficiency of quenching since they could hinder the phenolic hydrogen which was suggested to be a significant factor in the tocopherols quenching ability[92].

The purity data provided by Lubrizol states that the sample of this antioxidant provided has a much higher level of purity than the other two, around 96.5%, with the main impurity being methyl ester. Since this sample is of higher purity than the other two provided there is less margin for error in determining the RMM, which was estimated to be 390.6 $gmol^{-1}$.

One group of compounds that have also been studied for their singlet oxygen quenching efficiency are flavonoids, a group of naturally occurring polyphenolic compounds found in many foods[92]. Flavonoids are not only known for singlet oxygen quenching but also radical scavenging and reaction with the superoxide anion. The radical scavenging of hydroxyl and peroxyl radicals is of particular interest as this is another similarity to the phenolic antioxidant.

A comprehensive study by Tournaire *et al*.[93] found that for all of the flavonoids tested physical quenching was dominant over chemical quenching for singlet oxygen, which could suggest that the phenolic antioxidant may also be predominately a physical quencher. This effect was also seen by Nagai *et al*.[92] who studied various catechin derivatives, part of the flavonoid group of compounds, found in tea.

Another interesting conclusion of the flavonoid study was the control of the physical and chemical quenching efficiencies by different chemical features of the compound; with physical quenching being controlled by catechol moiety on the second ring while chemical quenching was controlled by the chemical structure of the third ring. Other studies have also found the importance of the chemical structures of further phenol rings being added[94,95].

The greater number of phenolic rings appears to increase the quenching efficiency due to having a greater number of accessible hydroxyl groups as well as having a greater number of rings over which energy can be distributed to stabilise the compound post energy transfer.[92]

While these factors do not affect the phenolic antioxidant's quenching efficiency this information could be of interest when looking into potential ways of modifying the phenolic antioxidant to improve its efficiency. However, the main concern with adding more phenolic groups is the addition of multiple hydroxyl groups which may hinder the antioxidants' solubility in base oil stocks.

4.6. Lubrizol Sulfurized Olefin

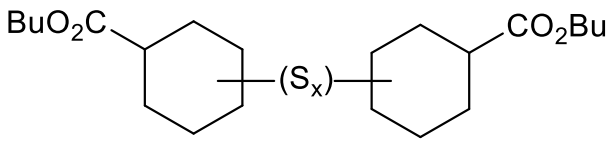


Figure 16 - Nominal Chemical Structure of Lubrizol Sulfurized Olefin

Figure 16 shows the main structure of the sulfurized olefin antioxidant provided to us by Lubrizol. However, this antioxidant is also the most varied as there is much less control in the production reaction, leading to a number of potential structures; such as the sulfur being potentially bonded at either carbon, or variations on the orientations of the chains. This also makes this antioxidant the most difficult to characterise due to the potential by-products which also increases the error in attempting to calculate an RMM value for the compound. However, this was done by taking the optimal compound structure, giving an estimation of the RMM of 408.4 $gmol^{-1}$.

A lot of studies have looked into the reaction of singlet oxygen with olefins, and other alkenes, since the double bonds within their structures are an easy point for oxidation attack. There have also been studies that look into the reaction of sulfides and sulfur-containing compounds with

there being evidence of sulfides being able to quench singlet oxygen by both physical deactivation and chemical reaction.

Jensen, Greer and Clennan[96] looked into the mechanism of reactions between singlet oxygen and sulfides and found that physical deactivation of singlet oxygen as well as chemical reaction occurred in aprotic solvents but that in protic solvents conversion to sulfurane by the solvent occurred.

From this information, it could be suggested that the sulfurized olefin may possibly exhibit both physical and chemical quenching of singlet oxygen, with the chemical quenching most likely to occur around the olefin structures of the compound while physical quenching is more likely to occur at the sulfurs.

4.7. Synergies

In a review paper by Kamal-Eldin and Appelqvist[81] the various mechanisms by which tocopherols work in synergy with other compounds are discussed. While not all of the mechanisms they discuss may apply to the other antioxidants tested, two of the mechanisms could potentially play a role in any synergies seen.

The first mechanism involves antioxidants that work by similar mechanisms to each other, in the review they discuss this in terms of anti-oxidation in general not just for singlet oxygen. However, the same principle could in theory be applied to the two mechanisms for singlet oxygen quenching, physical deactivation and chemical reaction. This mechanism could lead to a number of outcomes depending on which mechanism each of the antioxidants primarily quenches singlet oxygen. If both antioxidants primarily quench *via* the same mechanism, then they could potentially compete against each other to quench the singlet oxygen, leading to a higher overall level of quenching but smaller individual quenching efficiency. Alternatively, if they quench *via* different mechanisms then this could have a pronounced effect on the overall quenching as the two pathways may not compete to occur.

The second mechanism involves ‘regeneration’ of the primary antioxidant and would mainly occur if the antioxidant’s main mechanism for singlet oxygen quenching is by chemical reaction. With this mechanism, the secondary antioxidant returns the primary antioxidant to its original state and thus allows it to continue quenching the singlet oxygen, essentially allowing it to be recycled. This has been suggested as the potential mechanism for the synergy seen

between aminic and phenolic antioxidants in lubricants; with the phenolic antioxidant 'regenerating' the more potent aminic antioxidant.

This research considered the combined singlet oxygen quenching of three antioxidants and then comparing the data with the data compiled for the antioxidants when tested individually. If there are no synergistic properties displayed, then equation 16 will hold true. However, if this is not the case then it can be assumed that some process is occurring within the system which creates more efficient quenching than the potential quenching calculated from the individual systems.

Equation 16

Where;

k_q' – quenching constant for the primary antioxidant

$[Q']$ – concentration of the primary antioxidant

k_q'' – quenching constant for the secondary antioxidant

$[Q'']$ – concentration of the secondary antioxidant

k_q^S – quenching constant for the combined antioxidants

$[Q' + Q'']$ – concentration of the combined antioxidants

To determine whether any synergistic properties are being displayed is by looking at the effect of changing the concentration of one of the antioxidants while the second antioxidant concentration is held constant. By using this approach, it is possible to consider the effect of the second antioxidant as part of the solvent system and thus, by factoring in the individual quenching constant of the second antioxidant into the original calculation for the quenching constant (Equation 17), changes in the quenching capacity of the first antioxidant can be observed.

Equation 17

Where;

k'_q – the quenching constant of 1st quencher

k''_q – the quenching constant of 2nd quencher

$[Q'']$ – concentration of 2nd quencher

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ὼ Ὼ ὲ ὸ Ὼ ῖ ὼ Ὼ ή ὸ – from the plot of $A_0/\Delta A$ vs $[Q']$

k_d – the rate of quenching by the solvent

k_A - the rate of quenching by the acceptor compound

$[A]_0$ – the average starting concentration of the acceptor

By comparing the singlet oxygen quenching constants calculated both with and without a second antioxidant present it should give a clear indication as to whether the two antioxidants synergise with each other. If there is an apparent synergy between antioxidants, then by moving forward to characterise the system using chromatographic methods it should be possible to determine if this is due to them playing separate quenching roles or if a reaction is occurring between the two antioxidants yielding a more efficient quencher.

5. Experimental

5.1. Materials

The following materials were used throughout the experiments outlined ahead.

- Anthracene (Scintillation Grade, BDH Laboratory Reagents)
- 9,10-Dimethylanthracene (Reagent Grade, 99%, Sigma-Aldrich)
- Methylene Blue (Dye Content 89%, Sigma-Aldrich)
- Rose Bengal (93% Dye Content, Aldrich)
- Eosin Y (Technical, BDH Laboratory Reagents)
- Rubrene (Aldrich)
- Rhodamine B (BDH Laboratory Reagents)
- Zinc Phthalocycanine (Aldrich)
- Aluminium Phthalocycanine Chloride (Dye Content ~85%, Aldrich)
- Phthalocyanine (Dye Content 98%, Aldrich)
- OS42520U (Aminic Antioxidant, Lubrizol)
- OS207462F (Phenolic Antioxidant, Lubrizol)
- OC172911K (Sulfurized Olefin Antioxidant, Lubrizol)
- α-Tocopherol (≥95.5%, Sigma-Aldrich)
- Squalene (≥98%, Sigma-Aldrich)
- 1-Butanol (ACS Reagent Grade, ≥99.4%, Sigma-Aldrich)
- Hexadecane (Reagent Plus 99%, Sigma-Aldrich)

5.2. Developing the Method for Steady-state Measurements

To develop the method used for the main testing of the antioxidants throughout this project a number of smaller experiments were run. These included testing of different irradiation sources and filters, various sensitizing dyes, various solvents, two different acceptor compounds as well as whether to run in an open or closed system.

5.2.1. Production of Singlet Oxygen in Steady-state Experiments

For all of the steady-state experiments outlined in this section, where it is required, singlet oxygen was produced photo-chemically, *in situ*, using a sensitizing dye and an irradiating light source. A solution containing a sensitizing dye, an actinometer and the antioxidant/s being tested were irradiated in a quartz cuvette. To test if singlet oxygen was being produced the absorbance of the actinometer, which will readily react with any singlet oxygen present in the solution, was tested using UV-Vis spectroscopy on a HP 8450 UV/Vis diode array spectrophotometer. A decrease in the absorbance after irradiation gave a positive indication that singlet oxygen is being produced.

5.2.2. Open or Closed Cuvette for Testing

Anthracene (18 mg, 4.048×10^{-3} moldm^{-3}) and methylene blue (4 mg, 4.279×10^{-4} moldm^{-3}) were individually dissolved in methanol (25cm^3). The solutions were then further diluted 1 in 10 with methanol. Methylene blue and anthracene were combined in a 1:1 ratio and this mixture was transferred to a closed quartz cuvette for testing. The mixture was irradiated using a 250W Xenon arc lamp for twenty minutes and was measured at 355 nm, for anthracene, and 656 nm, for methylene blue, every two minutes during irradiation. This process was then repeated without closing off the cuvette. Both runs were run in triplet to confirm the results.

5.2.3. Testing Different Acceptor Molecules

9,10-Dimethylanthracene (2.2 mg, 2.152×10^{-4} moldm^{-3}) and methylene blue (4 mg, 4.279×10^{-4} moldm^{-3}) were individually dissolved in methanol (25 cm^3) and the methylene blue diluted by a factor of ten. The solutions were combined in a 1:1 ratio and transferred to a quartz cuvette for testing. The same process for testing was used as with previous tests with the anthracene and methylene blue solution, with measurements taken at 378nm instead of 355nm for 9,10-dimethylanthracene.

5.2.4. Testing Filters

After initial testing with 9,10-dimethylanthracene showed an issue with the xenon arc lamp irradiation source causing the 9,10-dimethylanthracene to self-sensitize a series of light filters were tested in an attempt to eliminate this issue. A solution containing 9,10-dimethylanthracene ($3.3x10^{-4}$ $moldm^{-3}$) was prepared and irradiated for twenty minutes using the xenon arc lamp with measurements taken at two minute intervals. This was repeated using a red filter (300 – 700 nm) and a yellow filter (up to 500nm). The filters were also tested using anthracene ($4.07x10^{-4}$ $moldm^{-3}$) as the acceptor molecule and methylene blue ($2.2x10^{-5}$ $moldm^{-3}$) as the sensitizer.

5.2.5. Testing Different Irradiation Sources - Xenon Arc Lamp vs LED Torch vs LED Lamp

In another attempt to avoid the issue of self-sensitization of the 9,10-dimetylanthracene other potential irradiation sources were proposed in the form of an LED torch (200 lumen, RS Components) and later an LED lamp (5W). To test these as possible replacements of the irradiation source for the xenon arc lamp test solutions of 9,10-dimethylanthracene ($3.5x10^{-4}$ $moldm^{-3}$) and methylene blue ($1.15x10^{-5}$ $moldm^{-3}$) were made up in methanol. The samples were then irradiated using the LED torch and the LED lamp using the same method as the xenon arc lamp; twenty minutes irradiation made up of two minute intervals for measurements to be taken. The initial tests were conducted without the use of a filter. A solution of 9,10-dimethylanthracene ($3.5x10^{-4}$ $moldm^{-3}$) in methanol was also made up for testing without a sensitizer to test for self-sensitization.

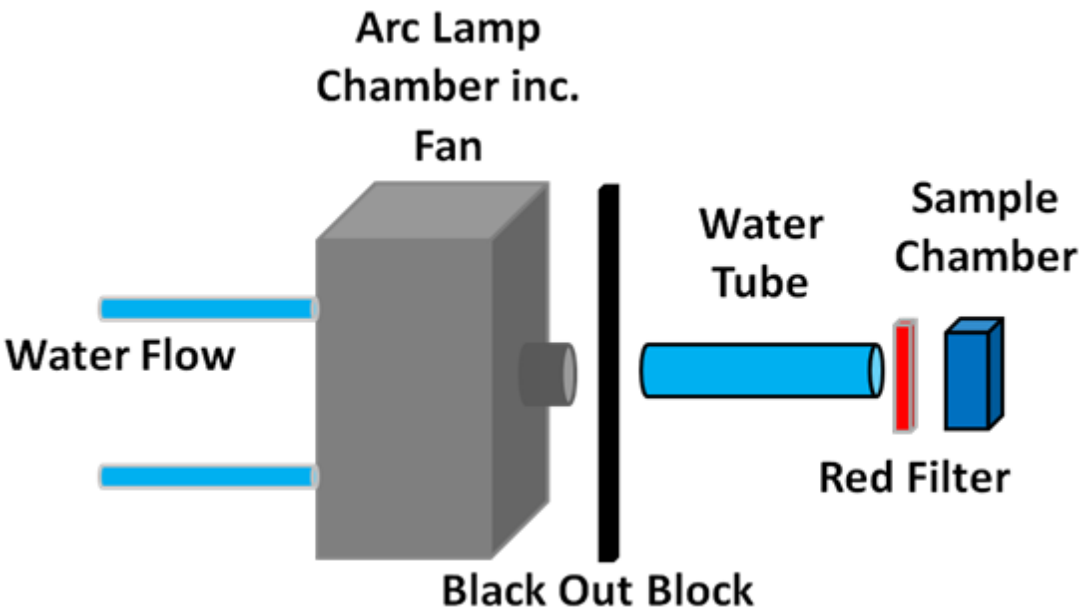


Figure 17 - Diagram Showing Arc Lamp Set-up for Experiments

For the LED torch and LED lamp it was possible to contain the experiment in a dark box to ensure that no other potential light sources would affect the sample.

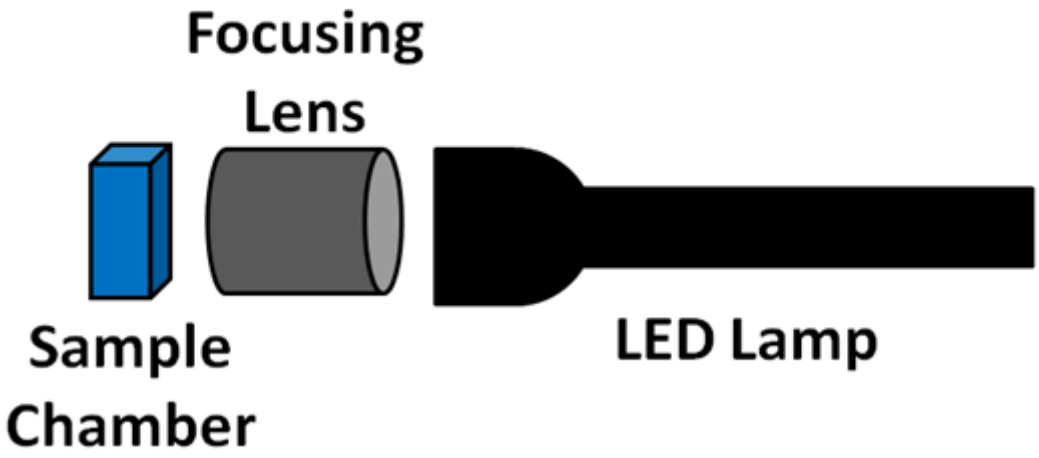


Figure 18 - Diagram Showing LED Torch Set-up for Experiments

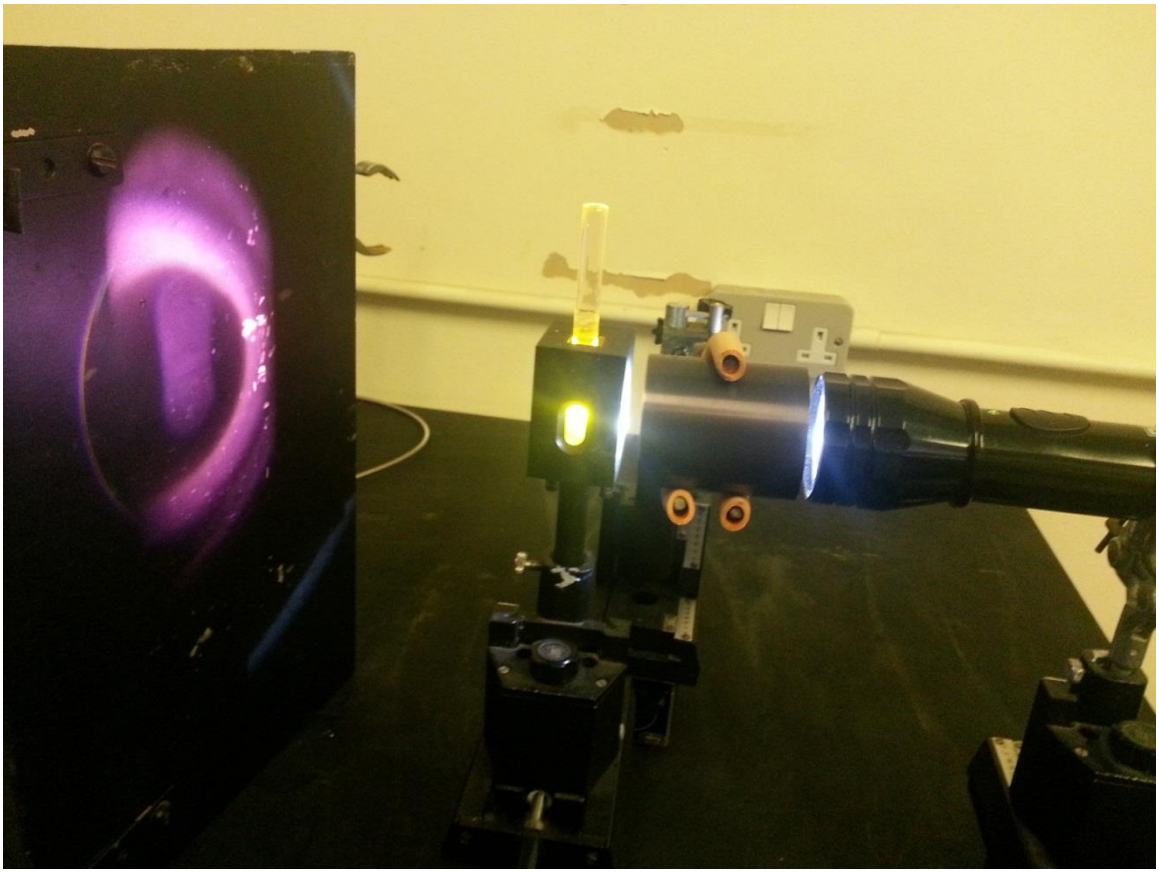


Figure 19 - LED Torch Set-up (Rhodamine 6G as Sample)

The set-up for the LED lamp identical to the set-up for the LED torch using the sample chamber and the focusing lens.

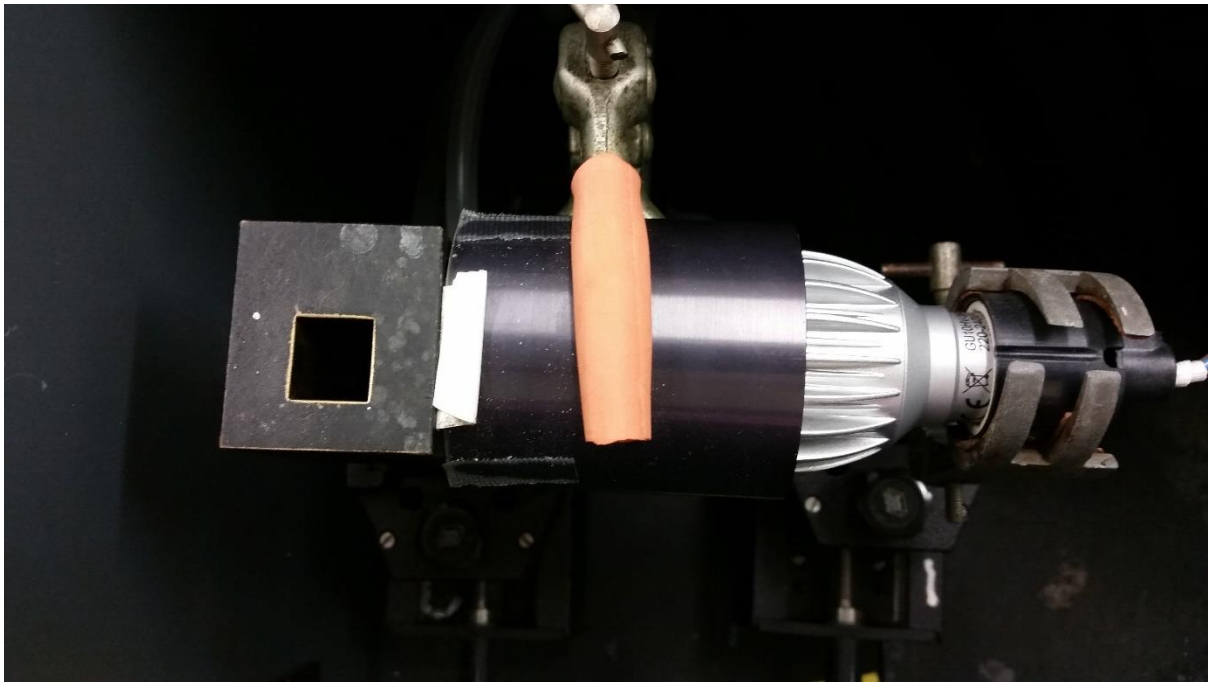


Figure 20 - LED Lamp Set-up

5.2.6. Solvent Tests for Antioxidants and Sensitizers

Both polar and non-polar solvents were tested for their ability to dissolve many of the potential compounds to be used in this research, including the three antioxidant samples provided by Lubrizol as well as a range of potential sensitizers. All of solvents tested were organic in nature since this fit with the nature of the conditions that the Lubrizol antioxidants would normally be used in.

The solvents used for testing are shown in table 4 below.

Table 4 - Solvents Tested with Antioxidants and Sensitizers

	Solvent
Polar	Methanol
	Acetonitrile
	1-Butanol
	1-Octanol
	1-Decanol
	Acetone
Non-polar	Hexadecane
	Toluene

The sensitizers tested included;

- Methylene blue
- Rose bengal
- Rubrene
- Phthalocyanine
- Aluminium phthalocyanine chloride

The antioxidants were tested at a concentration relative to the maximum concentration that they were to be tested at; 5 mg/ml, 50 mg/ml and 50 mg/ml for the aminic, phenolic and sulfurized olefin, respectively. Concentrations that would give an absorbance of approximately 1.0 were made up for each of the sensitizers, these were approximated using literature values for their respective molar absorption coefficients that were available.

5.2.7. Molar Absorption Coefficients

Molar absorption coefficients were calculated by making up stock solutions in methanol (100 cm^3) of anthracene (3.55 mg, $1.99x10^{-4}$ $moldm^{-3}$) and 9,10-dimethylanthracene (3.12 mg, $1.51x10^{-3}$ $moldm^{-3}$), and then diluting, by factors of 1 through 10. A methylene blue stock in methanol was made up (3.75 mg, $1.00x10^{-4}$ $moldm^{-3}$) and diluted by a factor of 10 before diluting for measurements.

Molar absorption coefficients were also calculated for methylene blue and 9,10-dimethylanthracene in 1-butanol using the same conditions.

5.2.8. Testing Sensitizers for Use with Sulfurized Olefin Antioxidant

A range of potential sensitizers, see table 4, were tested for reaction with the sulfurized olefin antioxidant provided by Lubrizol. Two sets of solutions containing enough of each sensitizer to produce an obvious colour were made up in 1-butanol in small vials and 25 drops of sulfurized olefin were added before the vials were sealed. A 'blank' solution containing only the sulfurized olefin antioxidant and no sensitizer was also made up to see if there was any visible change to just the sulfurized olefin.

One set of solutions was wrapped in tin foil and placed inside a dark cupboard while the second set was left uncovered on a bench-top. The solutions were left in these conditions for 7 days, after which visible observations were made of any changes to the colour of the solutions.

Table 5 - Singlet Oxygen Quantum Yields of Sensitizers Tested

Sensitizer	$^1O_2$ Quantum Yield from Literature REFERENCE
Rose Bengal	0.886
Rhodamine B	0.016
Eosin Y	0.440
Methylene Blue	0.600
Rubrene	0.500

5.3. Measuring Individual Quenching Constants Under Steady-state Conditions

Throughout this project concentrations were initially calculated in mg/ml (and are displayed as such) since the potential for impurities within the commercial samples made it impossible to determine the exact concentration in $moldm^{-3}$. However, for most of the results the concentration in $moldm^{-3}$ was estimated; although, in some cases the concentrations were reported in mg/ml still as to facilitate the transfer of knowledge from this work into a commercial environment where the use of mg/ml over $moldm^{-3}$ for reporting concentration was deemed more applicable.

Stock solutions of methylene blue (1.37 mg, $4.28x10^{-5}$ $moldm^{-3}$), zinc phthalocyanine (6.00 mg, $1.75x10^{-4}$ $moldm^{3}$) and 9,10-dimethylanthracene (6.19 mg, $3x10^{-4}$ $moldm^{3}$) were made up separately in 1-butanol (100 cm^{3}). These stock solutions were made up to be three times more concentrated then the final testing concentration to allow for easy preparation of the test samples.

Stock solutions of the various antioxidants were made up to give three times the maximum concentration used for testing as shown in table 6. From these stocks solutions at a range of concentrations were made for testing, see table 7 for the range of concentrations tested for each antioxidant. At least five different concentrations were tested for each antioxidant.

Table 6 - Concentrations and Weights of Antioxidants Used for Stock Solutions

Antioxidant	Concentration of Stock Solution ($moldm^{-3}$)	Weight Used For Stock Solution (mg/ml)
Aminic	$7.2x10^{-2}$	30
Phenolic	$3.6x10^{-1}$	150
Sulfurized Olefin	$3.66x10^{-1}$	150
α-Tocopherol	$6.9x10^{-3}$	3
Squalene	$1.83x10^{-1}$	75

Table 7 - Concentration Ranges Used for Calculating Quenching Constants

Antioxidant	Final Concentration Range ($moldm^{-3}$)
Aminic	$1.2x10^{-2} – 2.4x10^{-2}$
Phenolic	$6.4x10^{-2} – 1.2x10^{-1}$
Sulfurized Olefin	$6.12x10^{-2} – 1.22x10^{-1}$
α-Tocopherol	$4.6x10^{-4} – 2.3x10^{-3}$
Squalene	$1.2x10^{-2} – 6.1x10^{-2}$

From these stock solutions, the final test solution could be made. The sensitizer, acceptor and antioxidant were combined in a glass sample vial in a 1:1:1 ratio (5 cm^3 of each solution). From this mixture, a sample was transferred into a quartz cuvette (1 cm path length) and was irradiated over a twenty to forty-five minute time period. The absorbance at 378 nm from the 9,10-dimethylanthracene peaks was measured at two minute intervals during the first twenty minutes of the irradiation period and at five minute intervals between twenty to forty-five minutes. Each concentration was repeated multiple times to increase the precision of the end values.

Since it was not reliable to use methylene blue as the sensitizer for testing with the sulfurized olefin, zinc phthalocyanine was used instead; the reasoning for which will be discussed in chapter 6. So that a comparison could be made between the data obtained for the other antioxidants using methylene blue the aminic antioxidant was also tested using the zinc phthalocyanine sensitizer.

Using the same concentrations as the experiment in 1-butanol, the process was repeated in hexadecane. Since methylene blue would not dissolve into cyclohexane, zinc phthalocyanine was used as the sensitizer for all of the tests in hexadecane. To ensure maximum amount of zinc phthalocyanine was dissolved into the solution, the stock solution was sonicated until there was no visible solid left.

5.4. Measuring Singlet Oxygen Quenching Using Singlet Oxygen Lifetime

A stock solution of zinc phthalocyanine ($2.54x10^{-5}$ $moldm^3$) was made up in 1-butanol and a stock solution of perinaphthenone ($8.17x10^{-5}$ $moldm^3$) was made up in hexadecane. Stock solutions of the five antioxidants were made up in both 1-butanol and hexadecane. From the stock solutions of the antioxidants various concentrations were made up within the ranges

shown in table 11 and 12. Perinaphthenone was used as the sensitizer for the samples in hexadecane while zinc phthalocyanine was used as the sensitizer for the samples in 1-butanol. The sensitizer and antioxidant solutions were combined and a sample transferred to a quartz cuvette.

A Surelite Continuum I-10, Nd:YAG laser was used to excite the solution. The luminescence of singlet oxygen at 1270nm was taken using a germanium detector, in a liquid nitrogen jacket. At least three measurements were taken for each sample, with a cool-down period between each to ensure that all molecules had returned to the ground state.

Table 8 - Concentrations for 1-butanol Tests

Antioxidant	**Concentration of Stock ($moldm^3$)**	**Concentration for Stock (mg/ml)**	**Concentration Range for Testing ($moldm^3$)**	**Concentration Range for Testing (mg/ml)**
Aminic	$1.19x10^{-2}$	5.0	$5.93x10^{-4}$ – $5.93x10^{-3}$	0.25 – 2.5
Phenolic	$2.56x10^{-1}$	100	$6.4x10^{-2}$ – $1.28x10^{-1}$	25 – 50
Sulfurized Olefin	$2.45x10^{-2}$ & $2.45x10^{-1}$	10 & 100	$6.12x10^{-3}$ – $1.22x10^{-2}$ & $1.22x10^{-2}$ – $6.12x10^{-2}$	2.5 – 5 & 5 – 25
Squalene	$1.22x10^{-1}$	50	$1.22x10^{-2}$ – $6.09x10^{-2}$	5 – 25
α-tocopherol	$1.16x10^{-2}$	5.0	$1.16x10^{-4}$ – $5.80x10^{-4}$	0.05 – 1.0

Table 9 - Concentrations for Hexadecane Tests

Antioxidant	Concentration of Stock ($moldm^3$)	Concentration for Stock (mg/ml)	Concentration Range for Testing ($moldm^3$)	Concentration Range for Testing (mg/ml)
Aminic	$1.19x10^{-2}$	5.0	$5.93x10^{-4}$ – $5.93x10^{-3}$	0.25 – 2.5
Phenolic	$2.56x10^{-1}$	100	$6.4x10^{-2}$ – $1.28x10^{-1}$	25 – 50
Sulfurized Olefin	$4.90x10^{-2}$ & $2.45x10^{-1}$	20 & 100	$1.47x10^{-2}$ – $2.45x10^{-2}$ & $1.22x10^{-2}$ – $6.12x10^{-2}$	6 - 10 & 5 – 25
Squalene	$1.22x10^{-1}$	50	$1.22x10^{-2}$ – $6.09x10^{-2}$	5 – 25
α-tocopherol	$1.16x10^{-2}$	5.0	$1.16x10^{-4}$ – $5.80x10^{-4}$	0.05 – 0.25

5.5. Investigating Potential Synergistic Effects Between Antioxidants

Two different methods were attempted to try and investigate any synergistic effects between the various antioxidants previously tested.

Table 10 - Ratios of Antioxidants Used in Synergies Tests – Method 1

	AO 1	AO 2	AO 1	AO 2	AO 1	AO 2	AO 1	AO 2	AO 1	AO 2	AO 1	AO 2
Ratio	100	0	80	20	60	40	40	60	20	80	0	100
Concentration ($moldm^3$)	0.05	0	0.04	0.01	0.03	0.02	0.02	0.03	0.01	0.04	0	0.05
Concentration for stock ($moldm^3$)	0.15	0	0.12	0.03	0.09	0.06	0.06	0.09	0.03	0.12	0	0.15
Moles in stock ($x10^{-4}$ mol)	7.5	0	6.0	1.5	4.5	3.0	3.0	4.5	1.5	6.0	0	7.5

The first method involved maintaining a constant overall concentration for the combined antioxidant solution ($5x10^{-2}$ $moldm^3$). The ratios, and thus the concentrations, of the antioxidants making up this solution were changed in each solution in accordance with table 9.

For this method, all five antioxidants previously tested individually were used in combination. The solutions were combined and tested in the same manner as the previous synergy testing method.

In the second method stock solutions of methylene blue, zinc phthalocyanine and 9,10-dimethylanthracene were prepared as per previous experiments. Solutions containing two out of three of squalene, aminic and phenolic antioxidant were also prepared in 1-butanol (5 cm^3). For each set of solutions, the concentration for one of the antioxidants was kept constant while the other was increased with each subsequent solution. Table 8 shows the concentrations or range of concentrations used for each set of solutions.

Table 11 - Synergy Testing Concentration Combinations – Method 2

Antioxidant Combination	Constant Antioxidant	Changing Antioxidant
Aminic/Phenolic	Phenolic ($6.4x10^{-5}$ $moldm^{-3}$)	Aminic ($1.2x10^{-5}$ – $2.4x10^{-5}$ $moldm^{-3}$)
	Aminic ($1.2x10^{-5}$ $moldm^{-3}$)	Phenolic ($6.4x10^{-5}$ – $1.2x10^{-4}$ $moldm^{-3}$)
Aminic/Squalene	Squalene ($1.2x10^{-5}$ $moldm^{-3}$)	Aminic ($1.2x10^{-5}$ – $2.4x10^{-5}$ $moldm^{-3}$)
	Aminic ($1.2x10^{-5}$ $moldm^{-3}$)	Squalene ($1.2x10^{-5}$ – $6.1x10^{-5}$ $moldm^{-3}$)
Phenolic/Squalene	Squalene ($1.2x10^{-5}$ $moldm^{-3}$)	Phenolic ($6.4x10^{-5}$ – $1.2x10^{-4}$ $moldm^{-3}$)
	Phenolic ($6.4x10^{-5}$ $moldm^{-3}$)	Squalene ($1.2x10^{-5}$ – $6.1x10^{-5}$ $moldm^{-3}$)

As with previous experiments, the three solutions were combined and a sample transferred to a quartz cuvette. The sample was irradiated for forty-five minutes with a measurement of the absorbance at 378 nm being taken every two minutes for the first twenty minutes, then every five minutes until the end.

5.6. Chromatographic Study into Singlet Oxygen Quenching

Gas chromatography was tested as a potential chromatographic method for characterising the samples. The GC tests were run on an Agilent 7820A GC with a 30m x 320µm x 0.25µm 5% phenyl 95% methyl HP5 column using nitrogen as the carrier gas. The settings used are shown below in table 6.

Table 12 - Gas Chromatography Settings

Injection	**0.1 µl**
Split	10:1
Carrier Gas Flow Rate	2ml/min
Oven Temperature (start)	75°C
Oven Temperature (end)	240°C
Oven Temperature (ramp)	15°C/min

Each component was tested separately; including the sensitizer, acceptor and each antioxidant, to give a baseline of what peaks appear for each compound.

Later mixtures some of the different components in various combinations were tested to see if there were any unexpected peaks appearing or noticeable changes in the spectra. Irradiated samples containing all three components, as well as some combinations of sensitizers were also tested under the same conditions.

5.7. Investigating Temperature Dependence of Singlet Oxygen Quenching

Stock solutions containing methylene blue (1.37 mg, 4.28×10^{-5} moldm^3) and 9,10-dimethylanthracene (6.19 mg, 3×10^{-4} moldm^3) were prepared separately in 1-butanol (100 cm^3). The solutions were then combined in a sample vial (5 cm^3 of each) and additional 1-butanol was added (5 cm^3).

A water-jacketed sample holder fed by a water bath was used to heat the sample to the desired temperature for testing. The same method of measurement was used as with earlier experiments. The temperatures tested ranged from 25ºC (298K) to 80ºC (353K). All temperatures were repeated at least three times.

A stock solution of the aminic antioxidant was prepared in 1-butanol (10 mg/ml). From this stock, solutions containing concentrations between 1.25 mg/ml and 7.5 mg/ml were prepared. The three solutions were combined as per previous experiments and placed into the sample chamber and left for five minutes to heat to temperature (80ºC). The sample was irradiated and measurements taken as previously.

5.8. Looking into Alternative Acceptor Molecules

1,4-Dimethylfuran (2.3×10^{-1} moldm^{-3}) was tested for its suitability as a potential alternative acceptor for use in steady-state testing using zinc phthalocyanine (1.75×10^{-4} moldm^3) as the sensitizer and 1-butanol as the solvent.

An initial sample of 1,4-dimethylfuran was irradiated for 50 minutes without a sensitizer to test its stability under the irradiation conditions. A sample was then irradiated for 120 minutes with measurements taken every 10 minutes at 290nm with the sensitizer present. A further sample using the same concentrations was irradiated for 350 minutes total, with measurements being taken every 10 minutes for the first 120 minutes.

6. Results and Discussion I: Developing the Method

6.1. Anthracene vs 9,10-dimethylanthracene

Overall there were pros and cons for the use of each potential acceptor compound. From the initial results obtained from testing using anthracene as the acceptor it was clear that over the time periods tested there was little change in the absorbance of anthracene. This would lead to poor results if used as the overall change between the starting and ending absorbance could be considered to be within the margin of error and therefore hard to discern if the change is due to reaction or just noise. Especially so in the presence of a quencher, since its presence would lessen the overall reaction between anthracene and singlet oxygen.

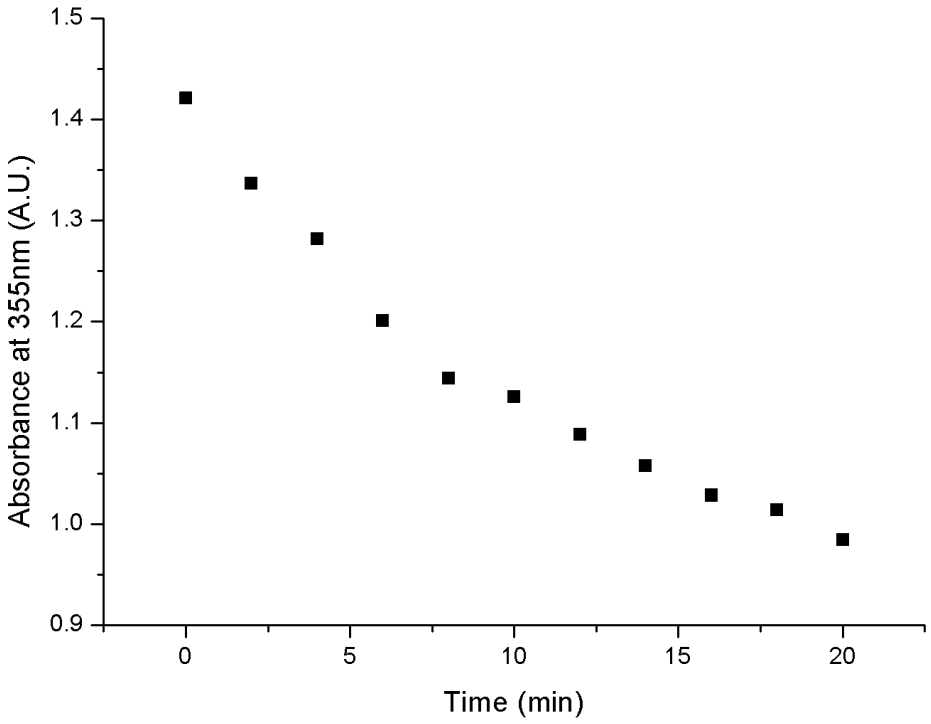


Figure 21 - Absorbance at 355nm vs Time for Anthracene

However, this slow reaction between anthracene and the singlet oxygen could be useful when considering testing over a prolonged period of time if there is a significant enough decline in the anthracene absorbance to justify that it is indeed due to a reaction.

With the 9,10-dimethylanthracene (DMA) on the other hand there was the opposite complication in that the DMA was disappearing at a higher rate than expected. The cause of

this unexpectedly fast drop off in DMA concentration was put down to the degradation of the DMA compound under the intensity of the xenon arc lamp used for irradiation at the time of the initial testing.

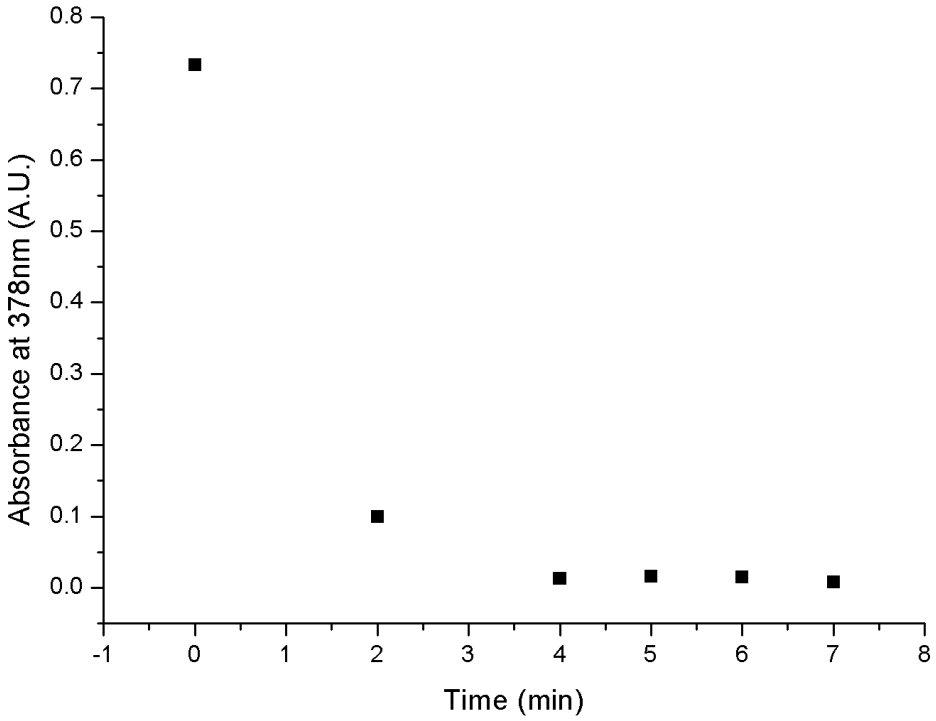


Figure 22 - Absorbance at 378nm vs Time for 9,10-dimethylanthracene

While this was a considerable problem, it was found that by passing the light through a red filter before the sample, across the wavelengths 300-700nm, the degradation of the DMA was lessened.

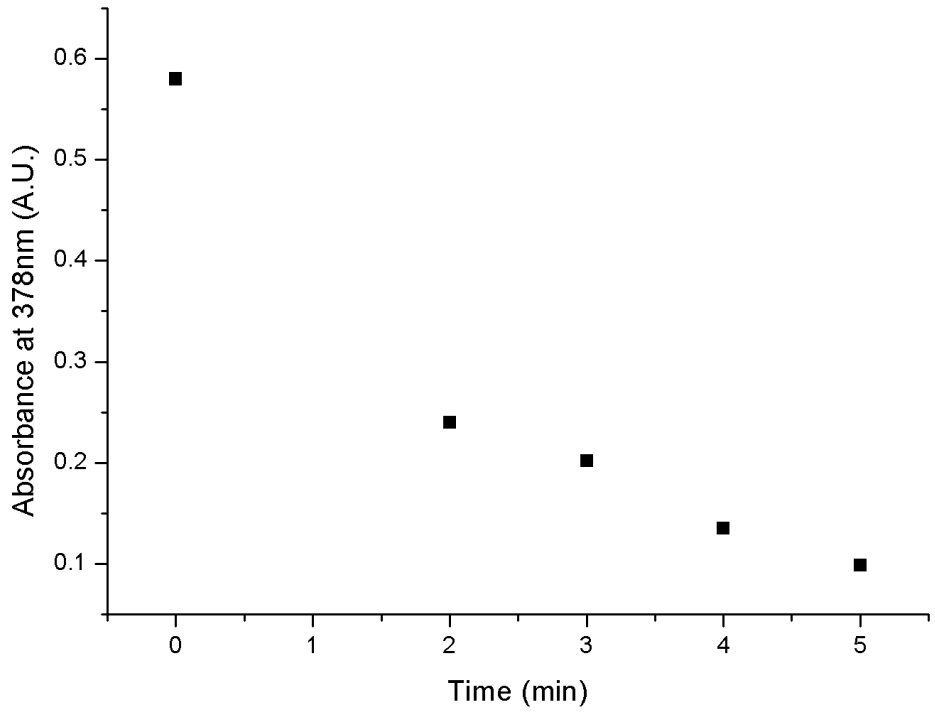


Figure 23 - Absorbance at 378nm vs Time for 9,10-dimethylanthracene with Red Filter

While there is still a strong disappearance over five minutes this is actually rather useful in that any changes in the rate of disappearance in the presence of a quencher should be very clear since the 9,10-dimethylanthracene is so readily reacting with singlet oxygen.

However, this was not a permanent solution as more accurate results would be obtained if there was no issue of degradation. As such other irradiation sources were investigated as the results of which are discussed later in this chapter.

6.2. Open System vs Closed System

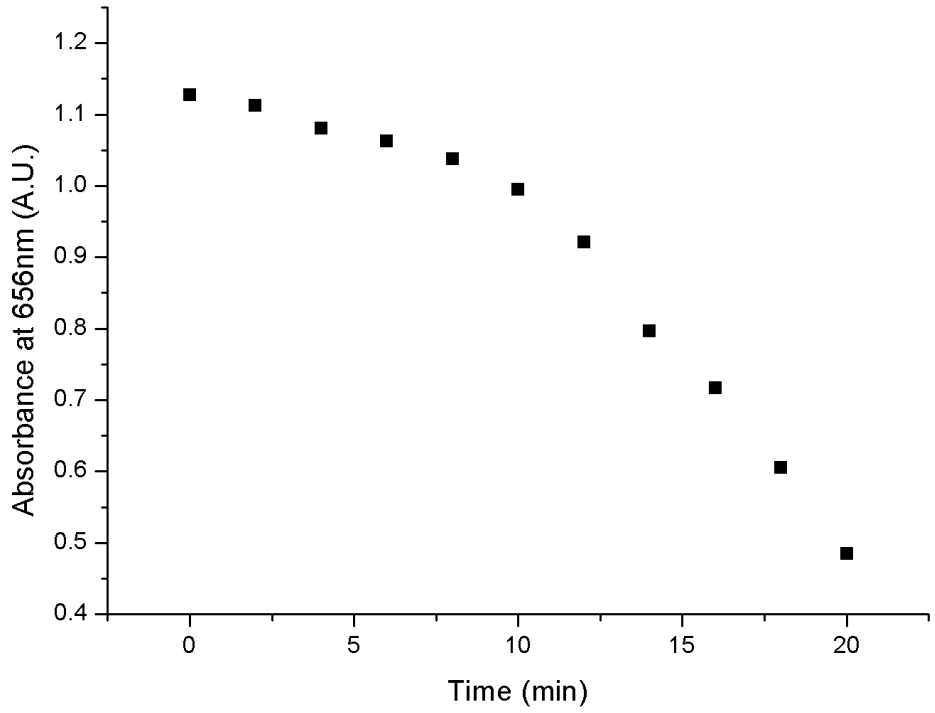


Figure 24 - Absorbance at 656nm vs Time for Methylene Blue in Closed Cuvette

The main issue found when running the experiment with a closed off cuvette was that the methylene blue absorbance dropped off significantly in a short time. This means that photo-bleaching of the dye has occurred and as such it is no longer able to react to produce singlet oxygen. This could also be due to the methylene blue converting to the colourless dimer which in turn could be detrimental to singlet oxygen production. Alternatively, it is possible that conversion to leuco-methylene blue, involving the transition of charge from the sulfur to the nitrogen, is occurring which is causing the loss of colour.

Figures 24 and 25 show the plots for the absorbance at 656nm, which corresponds with the absorbance of methylene blue. In a closed system, the drop off in the absorbance appears at around 10 minutes and decreases quite dramatically after this point. Meanwhile in an open system there is still a clear drop off a little later at around 14 minutes. Still seeing this drop off might suggest another issue that is causing the methylene blue absorbance to drop off, such as possibly being effected by the irradiation source.

Overall from this information it was decided to continue all future experiments in an open topped cuvette to allow sufficient air flow into the system to allow molecular oxygen to enter. It was also decided to look into alternative irradiation sources that were less intense as to avoid deterioration of the compounds whilst still being strong enough to generate the singlet oxygen.

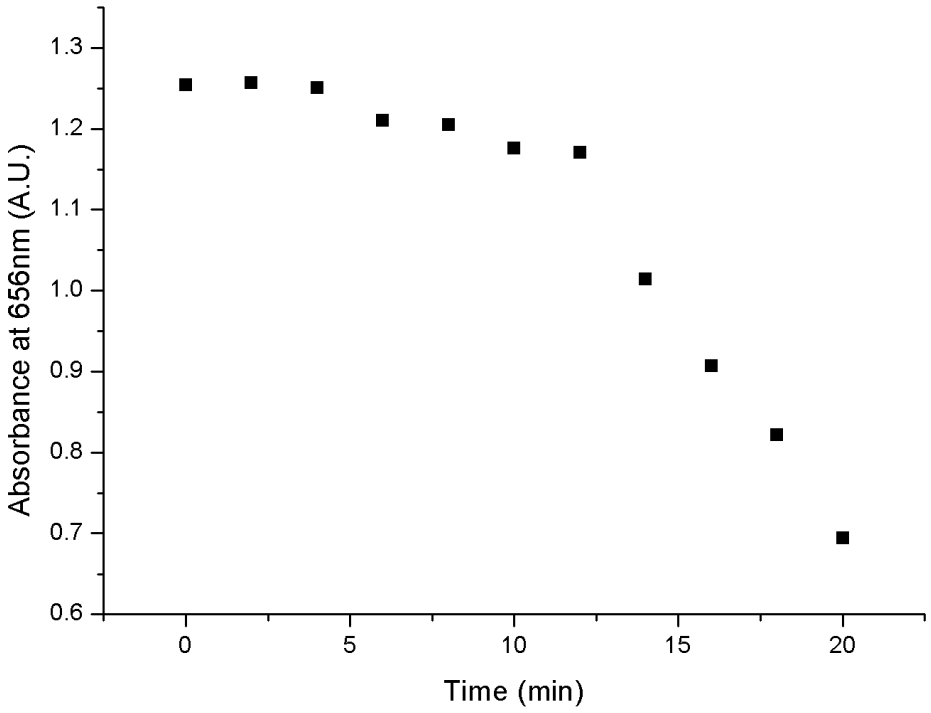


Figure 25 - Absorbance at 656nm vs Time for Methylene Blue in Open Cuvette

6.3. Arc Lamp vs LED Torch vs LED Lamp

It was clear after initial tests were conducted with the Xenon Arc Lamp as the light source that there were some potential complications. This was especially so in regards to using 9,10-dimethylanthracene as the acceptor under these conditions as it was observed that the DMA was absorbing too much from the light source and degrading as a result, thus yielding inaccurate results.

Table 13 - Concentration of 9,10-dimethylanthracene over Time with Irradiation from Xenon Arc Lamp

Time (min)	Concentration of DMA ($moldm^{-3}$)
0	1.1454
1	0.84997
2	0.70509
3	0.55468
4	0.48543
5	0.3793

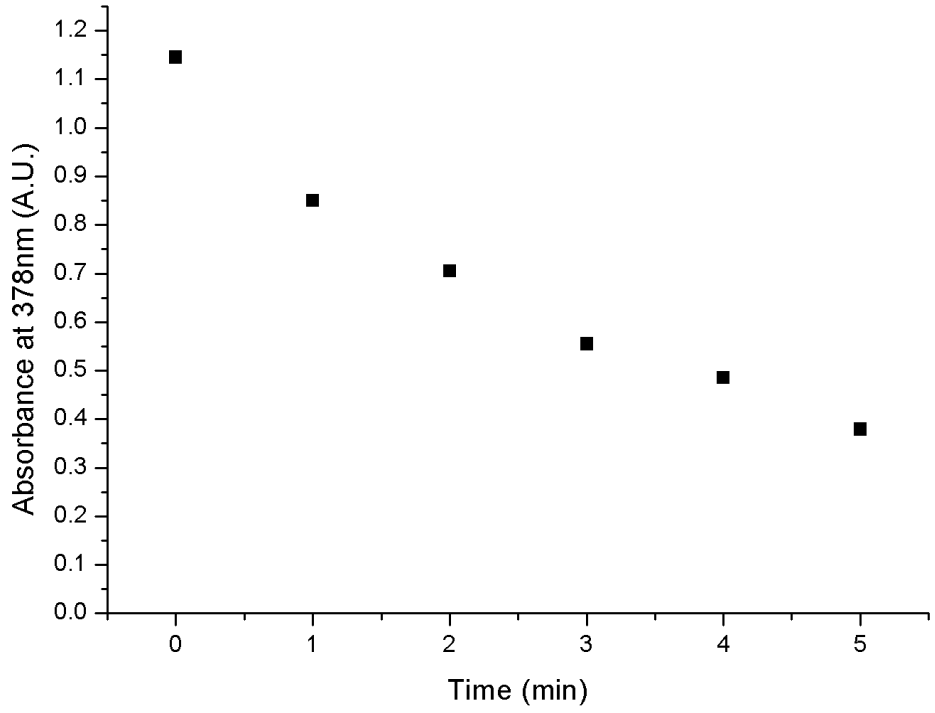


Figure 26 - Absorbance at 378nm vs Time for 9,10-dimethylanthracene with Xenon Arc Lamp Irradiation

As can be seen in table 13 and figure 26, the degradation of DMA under the Xenon arc lamp was a fast process, having a strong and constant effect on the concentration of DMA present from the first minute.

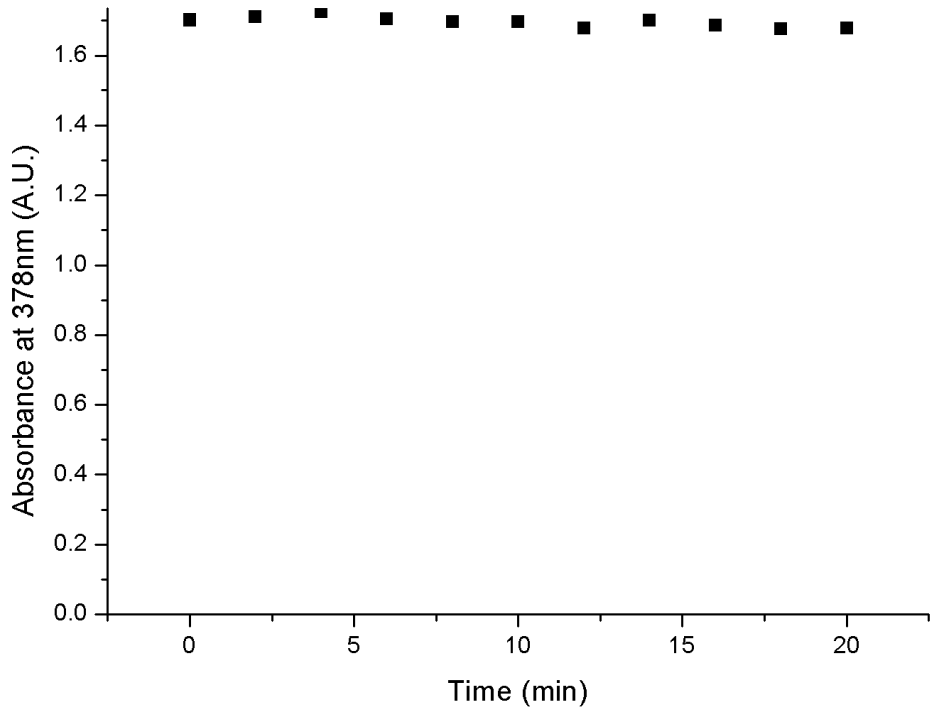


Figure 27 - Absorbance at 378nm vs Time for 9,10-dimethylanthracene with Irradiation from LED Torch

The experiments conducted using the LED torch as the light source appeared to resolve this issue as the LED light source was not producing enough energy in the appropriate wavelengths to cause degradation of the DMA, as seen above. However, a new issue was encountered in that the LED torch relied on batteries and would slowly decline in power output as the batteries were drained, as seen in figure 28. This meant that it was not possible to do prolonged runs without a drop off in the power output, which in turn would affect the singlet oxygen production rates and therefore the overall results.

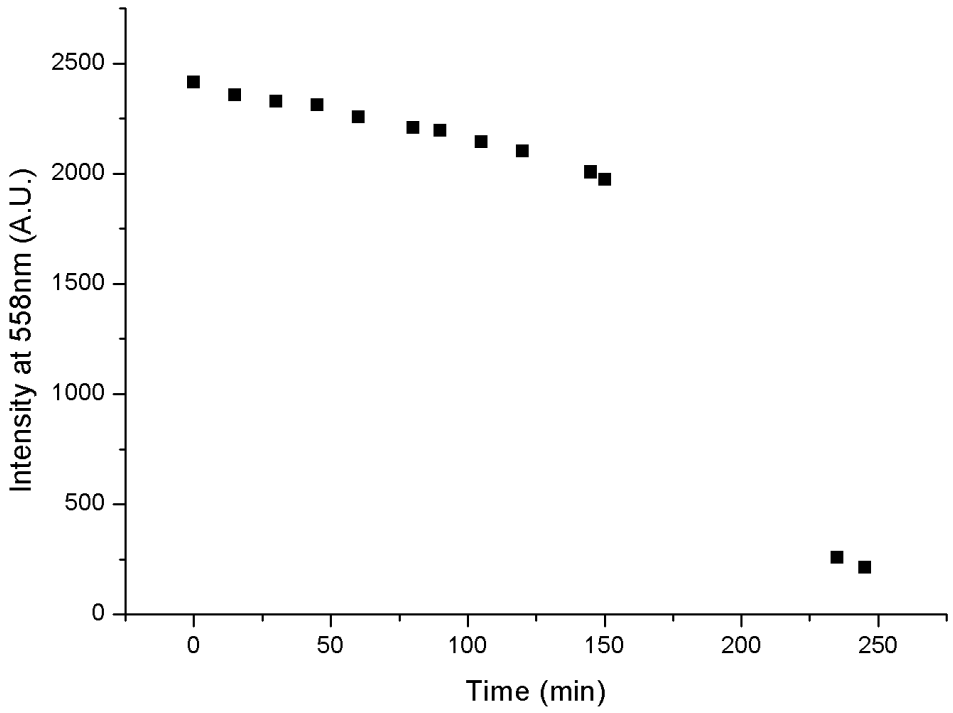


Figure 28 - Intensity at 558nm vs Time of Irradiation from LED Torch

A compromise was found in the use of an LED lamp as the light source since, being mains powered rather than relying on batteries, there was no issue with power output dropping off unexpectedly. Also, the power output in the wavelength range for DMA was low since the source was from an LED bulb.

6.4. Molar Absorption Coefficients

Plots of absorbance vs concentration were created for methylene blue, anthracene and 9,10-dimethylanthracene, with the slope being taken as the molar absorption coefficient. These values will be used in calculations for concentrations of these compounds from absorbance data.

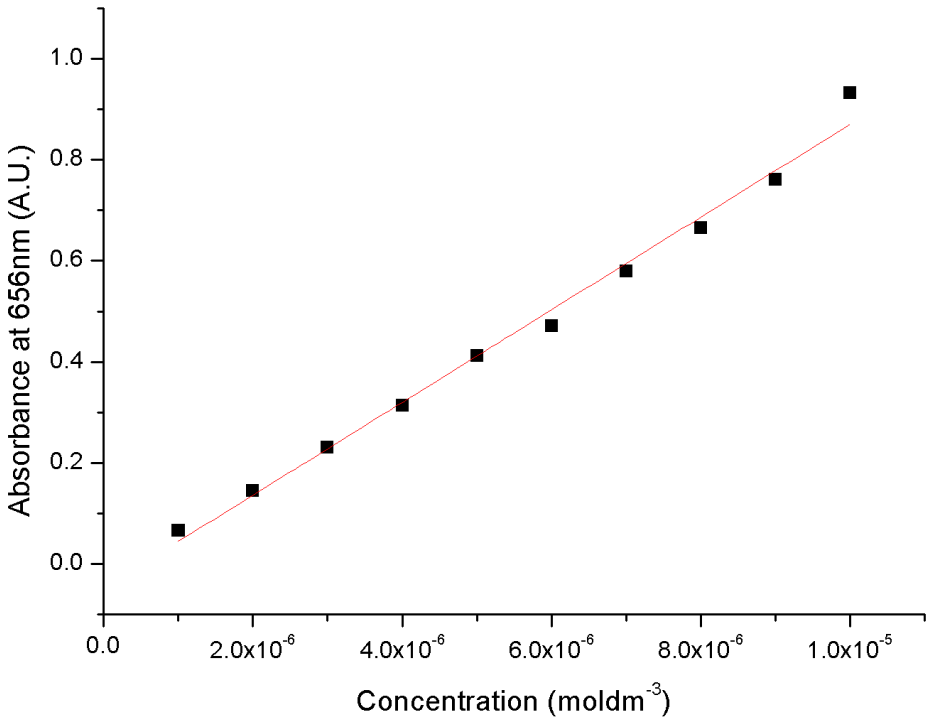


Figure 29 - Concentration vs Absorbance for Methylene Blue

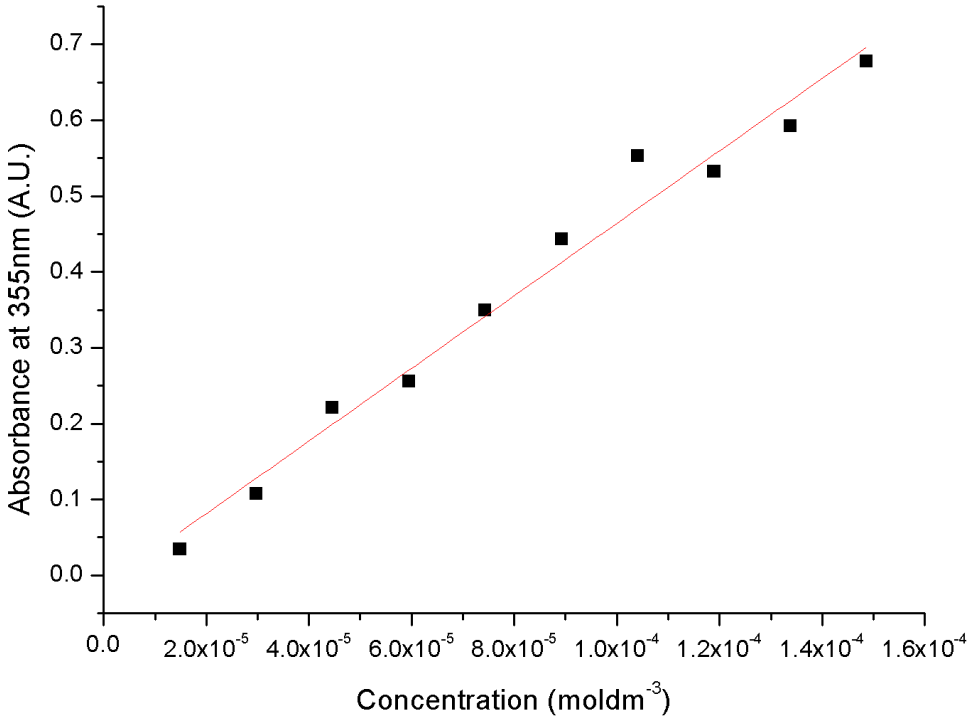


Figure 30 - Concentration vs Absorbance for Anthracene

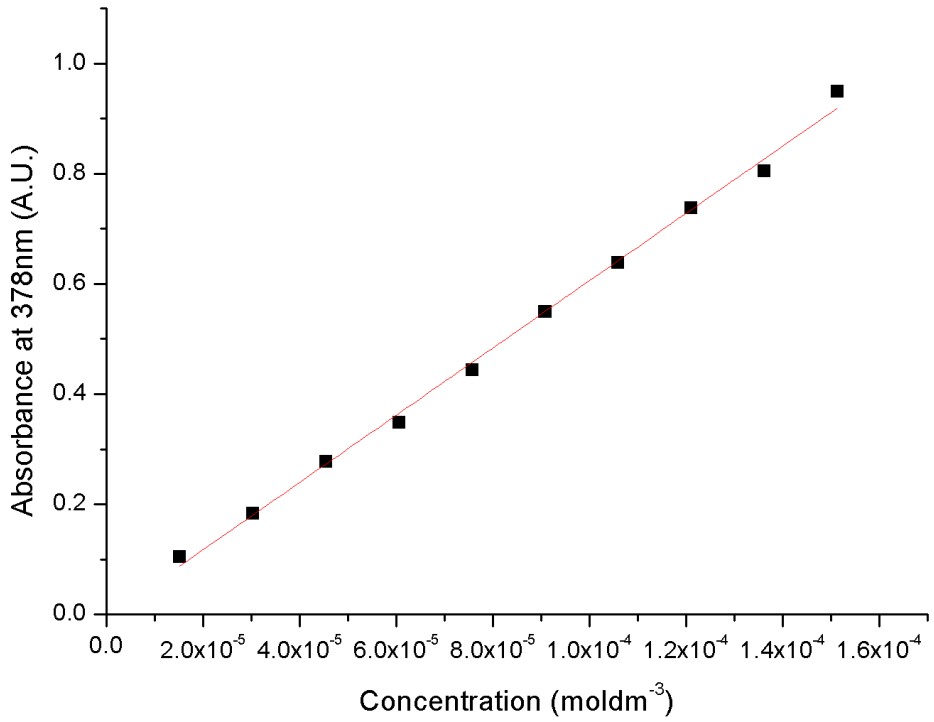


Figure 31 - Concentration vs Absorbance for 9,10-dimethylanthracene

Table 14 - Calculated Molar Absorption Coefficients

Compound	**Calculated ε value ($Lmol^{-1}cm^{-1}$)**
Methylene Blue	91779
Anthracene	4778
9,10-dimethylanthracene	6104

6.5. Sensitizers

When attempting to test the sulfurized olefin antioxidant using methylene blue as the sensitizer a problem with bleaching of the dye occurred. This only occurred when the sulfurized olefin was used at the higher concentrations; however, it was still within the desired testing concentrations for this antioxidant.

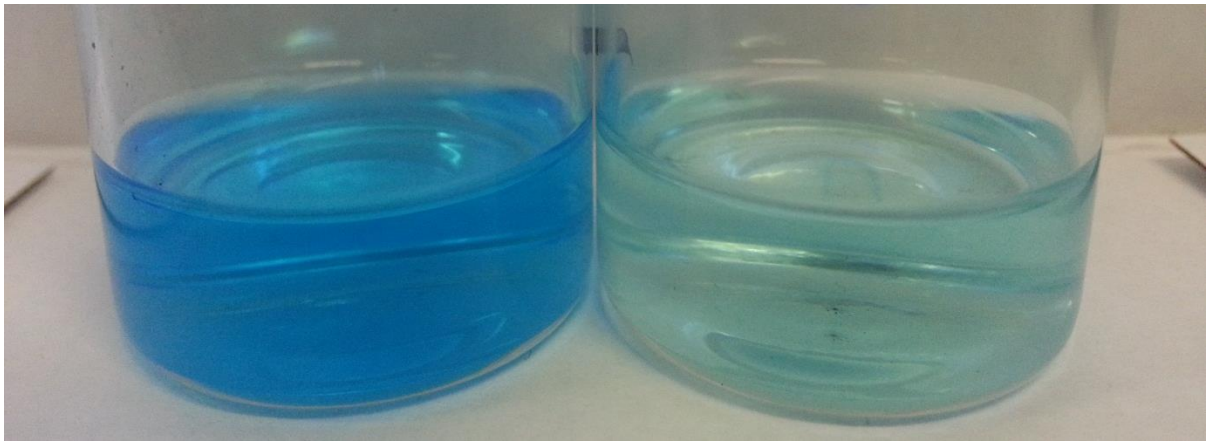


Figure 32 - Comparison of Low and High Concentrations of Sulfurized Olefin with Methylene Blue

Table 15 shows a breakdown of whether there was any photo-bleaching occurring for the sensitizers tested as well as their recorded singlet oxygen quantum yields as found in the literature[32]. These results can also be seen in figures 33 - 36, the sensitizers shown from right to left are in the same order as in table 15, with a blank containing only solvent for reference on the far right.

Table 15 - Results of Photo-bleaching Tests (in methanol/1-butanol)

Sensitizer	**$^1O_2$ Quantum Yield**	**Observed Bleaching (Light)**	**Observed Bleaching (Dark)**
Rose Bengal	0.886	P	O
Rhodamine B	0.016	O	O
Eosin Y	0.440	P	O
Methylene Blue	0.600	P	O
Rubrene	0.500	P	O

Figure 33 - Solutions Kept in the Light, Day 1

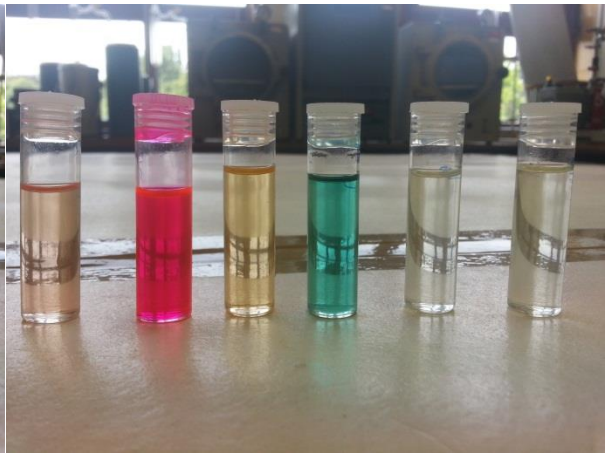


Figure 34 - Solutions Kept in the Light, Day 7

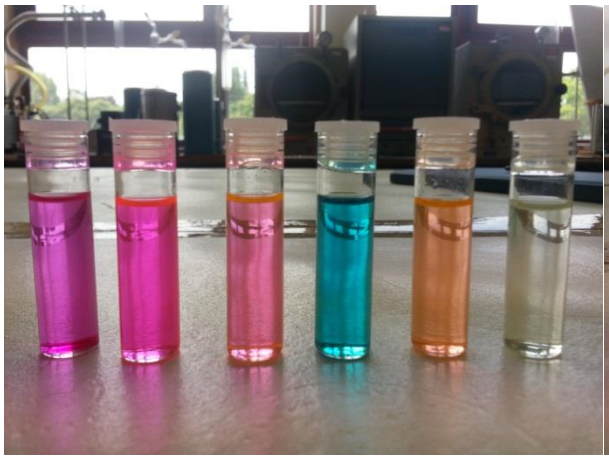


Figure 35 - Solutions Kept in the Dark, Day 1

Figure 36 - Solutions Kept in the Dark, Day 7

Another factor that was considered when comparing possible sensitizers was their absorption spectra. It was important that the sensitizer absorption did not have a strong crossover with the acceptor, 9,10-dimethylanthracene. This was especially true if there was any variation in the sensitizer's absorbance throughout a run as it could affect the observed absorbance of the acceptor and therefore affect the results obtained, making them less accurate and reliable.

The best of the initial sensitizers tested to avoid this as an issue was methylene blue; however, since this sensitizer had already been shown to have other issues it was not an ideal sensitizer to use.

Rose bengal, rhodamine B and eosin Y all had absorbance spectra that, while starting very close to the 9,10-dimethylanthracene peak, showed little to no potential cross-over that could significantly affect results. However, the literature showed that rhodamine B did not have a sufficient singlet oxygen quantum yield to be used for testing, so it was disregarded as a

potential sensitizer. The literature also gave a lower value for the singlet oxygen quantum yield of eosin Y than the other sensitizers, however, the value was still high enough for it to potentially be used for testing.

Zinc phthalocyanine was not included in these tests as it was suggested at a later point since it absorbed around the same wavelengths as methylene blue and basic tests showed no obvious reaction with the sulfurized olefin.

6.6. Solvents

Table 16 - Visual Observations of Antioxidants in Each Solvent

Antioxidant	Solvent				
	Methanol	Acetonitrile	Acetone	Hexadecane	Toluene
Lubrizol Aminic	~	O	P	P	P
Lubrizol Phenolic	P	P	P	P	P
Lubrizol Sulfurized Olefin	P	P	P	P	P

Table 17 - Visual Observations of Antioxidants in Each Solvent cont.

Antioxidant	Solvent		
	1-butanol	1-octanol	1-decanol
Lubrizol Aminic	P	P	P
Lubrizol Phenolic	P	P	P
Lubrizol Sulfurized Olefin	P	P	P

Table 18 - Visual Observations of Sensitizers in Each Solvent

Sensitizer	Solvent				
	Methanol	ACN	Acetone	Hexadecane	Toluene
Rose Bengal	P	P	P	O	O
Rubrene	~	~	~	P	~
Methylene Blue	P	P	P	O	O

Table 19 - Visual Observations of Sensitizers in Each Solvent cont.

Sensitizer	Solvent		
	1-butanol	1-octanol	1-decanol
Methylene Blue	P	P	P
Phthanolcyanine	O	O	O
Aluminium Phthalocyanine Chloride	P	P	P

Some issues were found in trying to dissolve the aminic antioxidant in methanol which, along with the substantial differences between methanol and the primary medium that the antioxidants would work within, was a main reason why it was decided to look into other solvents for the primary testing. This was despite the advantages of running samples in methanol since there is a plethora of data available from the literature in regards to previous similar testing that has been done.

It also appeared that the aminic antioxidant would not dissolve sufficiently into acetonitrile. Therefore, it was deemed an unsuitable solvent to use for further testing since it would not be possible to test one of the main samples.

Acetone was marked as a potential solvent due to it showing no issues dissolving any of the compounds tested. However, it still had the same issue of not being very similar to the engine oil medium and there were other non-polar solvents that were more suitable.

Hexadecane was marked as a potential solvent for further testing as it showed no issues dissolving the Lubrizol samples as well as one of the tested sensitizers and was also a good

comparison to the desired medium. However, its use did limit the number of possible sensitizers that could be used, rubrene being the only one of the sensitizers tested to dissolve. Since rubrene has been shown to not have a very high singlet oxygen quantum yield a different sensitizer would have to be used for further testing. As zinc phthalocyanine was deemed a useful sensitizer for use with the sulfurized olefin and it was found that it would dissolve sufficiently for testing in hexadecane, hexadecane was approved for use in later testing.

All three of the sensitizers used in the initial solubility tests were found to either have issues dissolving sufficiently to be used in testing or did not dissolve at all in toluene. However, all three of the Lubrizol samples dissolved without any issues. Therefore, if a suitable sensitizer could be found then toluene would potentially be a useful solvent to test in, especially since it sits relatively central in terms of polarity which would make for an interesting comparison between polar and non-polar solvent tests.

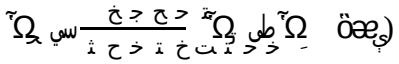
The only compound, of those tested, to show any issues dissolving in the longer chain alcohols was phthalocyanine. However, derivatives of the compound, including aluminium phthalocycanine chloride and zinc phthalocyanine, showed no issues. Of the longer chain alcohols 1-butanol was chosen as a suitable solvent to continue with in this project due to all the important compounds readily dissolving, as well as being a polar solvent similar enough to methanol and ethanol for comparison to data from the literature.

7. Results and Discussion II: Individual Quenching Constants

In this section the results pertaining to the quenching constants obtained for each individual antioxidant will be analysed and discussed. This will include comparisons between each of the antioxidants as well as a discussion of the two different methods and solvents tested during this research.

7.1. Steady-State Measurements

To calculate the overall singlet oxygen quenching constant, first a plot of $A_0/\Delta A$ vs [Q] is constructed, where A_0 is the starting absorbance of the acceptor, ΔA is the difference between the starting absorbance and the ending absorbance and [Q] is the concentration of the quencher being tested. From this plot, the slope and intercept can be inserted into equation 18 to give the final quenching constant, kg.



Equation 18

Where;

k_d – decay constant for singlet oxygen in the solvent

$k_{A'}$ – rate constant for the reaction between singlet oxygen and the acceptor

$[A']_0$ – starting concentration of the acceptor

The values for k_d and $k_{A'}$ were taken from previous studies that used similar or the same conditions as this study[32]

Table 20 - Alpha-tocopherol Full Data Set

[Q] (mold m^{-3})	A_0	ΔA	$A_0/\Delta A$	Avg A_0	Avg ΔA	Avg $A_0/\Delta A$	σ
4.64E-04	0.73507	0.43816	1.67763	0.73086	0.43967	1.66239	0.01519
4.64E-04	0.72943	0.43734	1.66788				
4.64E-04	0.72809	0.44351	1.64165				
9.29E-04	0.6773	0.31953	2.11968	0.67944	0.3151	2.15658	0.02879
9.29E-04	0.68021	0.31489	2.16015				
9.29E-04	0.6808	0.31088	2.18991				
1.39E-03	0.82717	0.24541	3.37056	0.86332	0.24796	3.48518	0.15177
1.39E-03	0.8769	0.25903	3.38532				
1.39E-03	0.88588	0.23945	3.69965				
1.86E-03	0.82305	0.19362	4.25085	0.84669	0.20588	4.13555	0.36476
1.86E-03	0.85399	0.2292	3.72596				
1.86E-03	0.86302	0.19482	4.42983				
2.32E-03	0.95674	0.17987	5.31906	0.94450	0.16973	5.64446	0.59757
2.32E-03	0.93119	0.16269	5.72371				
2.32E-03	0.96053	0.14252	6.73962				
2.32E-03	0.92955	0.19384	4.79545				

Table 20 shows the overall results obtained for α-tocopherol across all of the concentrations tested. Table 21 below shows the data used to plot the graph $A_0/\Delta A$ vs [Q] from which the quenching constant was calculated which is shown in Figure 37.

Table 21 - Alpha-tocopherol Plot Data

A_0 (A.U.)	ΔA	$A_0/\Delta A$	[Q] ($moldm^{-3}$)	$[A']_0$ ($moldm^{-3}$)
0.73086	0.43967	1.66239	4.64E-04	$1.197x10^{-4}$
0.67944	0.3151	2.15658	9.29E-04	$1.113x10^{-4}$
0.86332	0.24796	3.48518	1.39E-03	$1.414x10^{-4}$
0.84669	0.20588	4.13555	1.86E-03	$1.387x10^{-4}$
0.94450	0.16973	5.64446	2.32E-03	$1.547x10^{-4}$

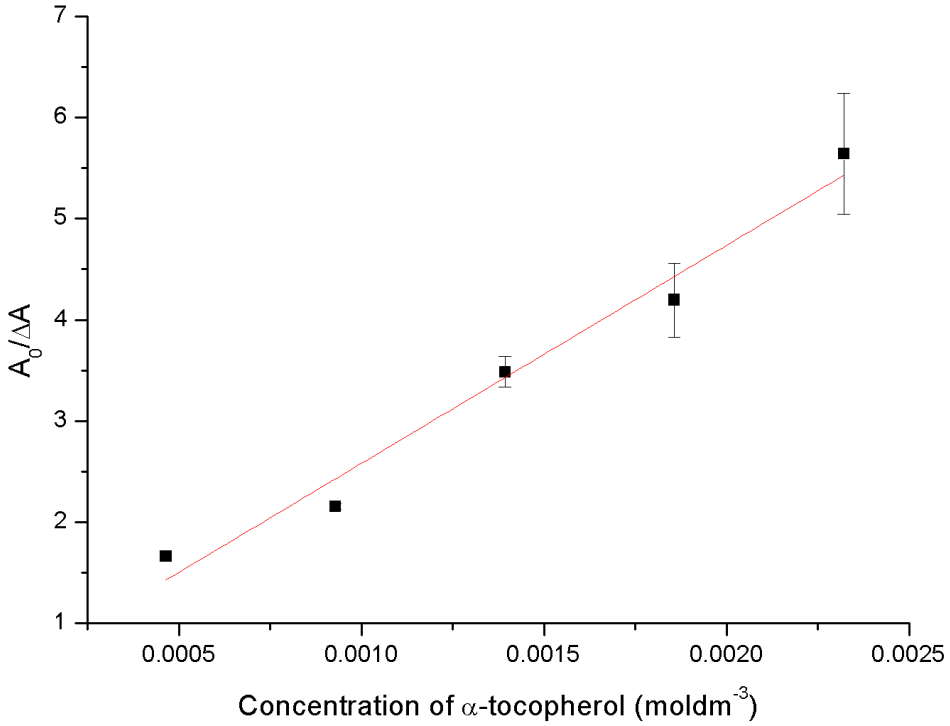


Figure 37 - Alpha-tocopherol Steady-state (in 1-butanol)

Table 22 - Alpha-tocopherol Steady-state

	Value
Intercept	0.42774
Slope	2154.51149 dm^3mol^{-1}

Taking these values and putting them into the equation yields;

$$\frac{\varsigma\ \rho\ \tau\rho\ \rho\ \tau\ \omega}{\pi\ \varsigma\ \chi\ \chi\ \tau}\ \upsilon\ \varsigma\ \pi\ \pi\ \pi^{2}$$

$$\varsigma\ \psi\ \chi\ \pi\ \varsigma\ \chi\ \tau\ \sigma\ \varsigma$$

Table 23 - Calculated Quenching Constants for All Antioxidants Across All Conditions

Quencher	**Steady State k_q /$dm^3mol^{-1}s^{-1}$ (1-butanol)**	**Steady State k_q /$dm^3mol^{-1}s^{-1}$ (hexadecane)**	**Lifetime k_q /$dm^3mol^{-1}s^{-1}$ (1-butanol)**	**Lifetime k_q /$dm^3mol^{-1}s^{-1}$ (hexadecane)**	**k_q /$dm^3mol^{-1}s^{-1}$ from literature (ethanol)**
Sulfurised Olefin (ZnPh)	$1.94x10^5$	2.58×10^6	$6.65x10^5$	3.55×10^5	
Phenolic	$2.31x10^5$	N/A	$2.06x10^6$	7.23×10^5	
Aminic	1.28×10^7 (ZnPh) $2.54x10^7$ (MB)	1.03×10^7	$5.65x10^6$	4.70×10^6	
Squalene	$3.18x10^6$	6.14×10^5	$2.84x10^6$	1.96×10^6	$4.20x10^6$
α-tocopherol	$2.87x10^8$	1.82×10^6	$1.19x10^8$	5.95×10^7	$2.10x10^8$

As can be seen in table 23 the results in 1-butanol from both the steady-state and lifetime methods for α-tocopherol both came out within the same order of magnitude to the results obtained from literature. This gave confidence in the accuracy of both methods. This also appeared to be true for the results obtained for Squalene, adding to the confidence in the methods.

Since α-tocopherol shows such significant quenching, a comparably small concentration was required in testing to show enough change in the rate of reaction between the 9,10-dimethylanthracene and singlet oxygen to determine the quenching rate constant. Through the repeated testing at various concentrations it was possible to obtain values that were in strong agreement with each other.

Comparing the singlet oxygen quenching constant, k_q, shown in table 23, to values found in literature under similar conditions[32] of 2.10×10^8 $dm^3mol^{-1}s^{-1}$ it can be seen that the values are very similar. Taking into consideration that there may be slight differences in the two methods used, these values appear to be in strong agreement with one another, giving confidence to the accuracy of the steady-state testing method for calculating the singlet oxygen quenching constant for α-tocopherol.

7.1.1. Aminic

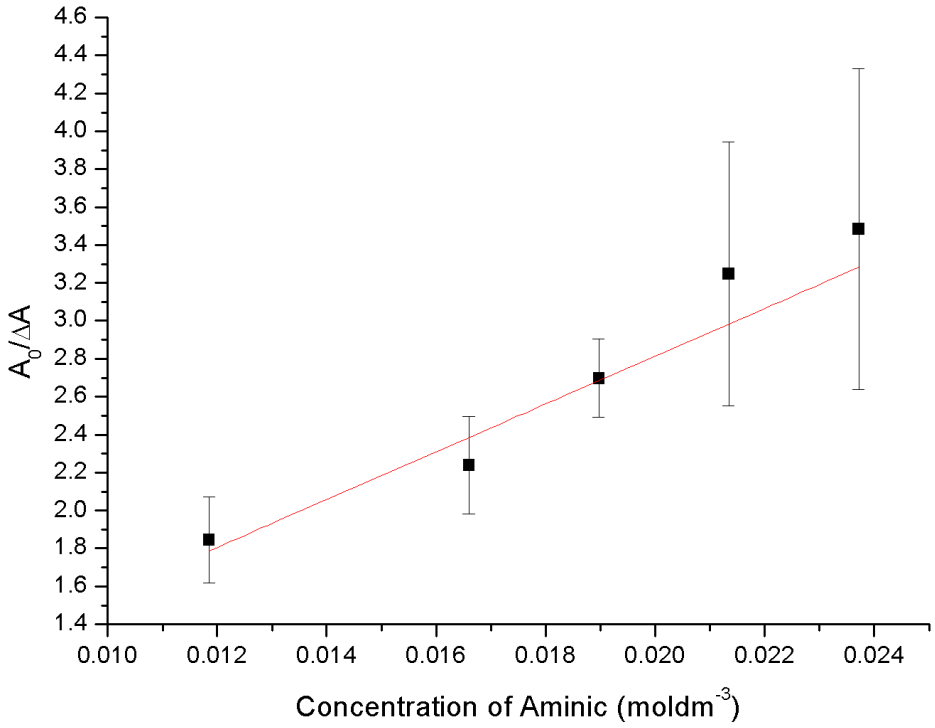


Figure 38 - Aminic Steady-state (Methylene Blue as Sensitizer, in 1-butanol)

Table 24 - Aminic Steady-state (Methylene Blue as Sensitizer, in 1-butanol)

Adjusted R-Square	0.93086
	Value
Intercept	0.29428
Slope	126.02416 dm^3mol^{-1}
Calculated k_q	2.54 x 10^7 $dm^3mol^{-1}s^{-1}$

The results obtained for the aminic sample did, within the error, show linear positive trend between $A_0/\Delta A$ and the concentration of the antioxidant.

Interestingly, the calculated singlet oxygen quenching constant is relatively high, showing that the aminic antioxidant to be a good quencher of singlet oxygen as well as suggesting its strength as an antioxidant. This conclusion is in keeping with the results that were expected from the Lubrizol sample, since the aminic antioxidant is known by Lubrizol as an efficient antioxidant within their lubricant additive formulations.

Jiang *et al*[97] also looked into the reaction between various nitrogen containing compounds, in this case secondary amines, and singlet oxygen. This research is of great interest due to the similarity in structure of some of the compounds tested, figure 39 and 40.

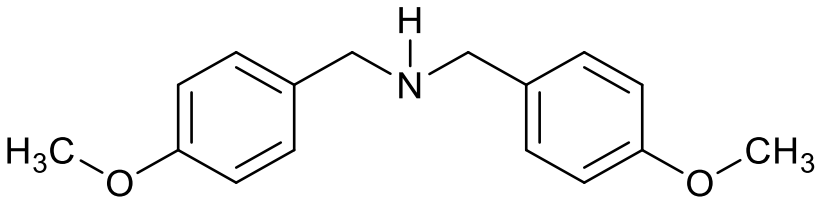


Figure 39 - Compound 1b from Jiang et Al[97]

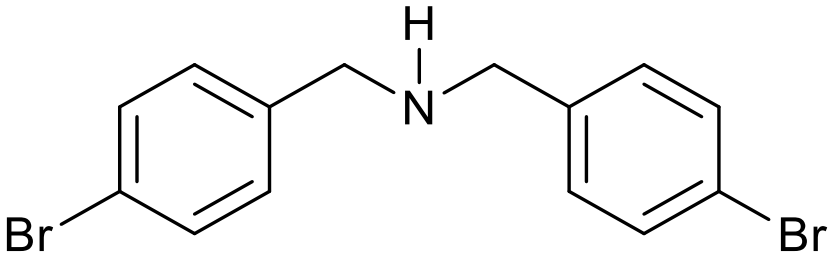


Figure 40 - Compound 1c from Jiang et al[97]

The research showed these compounds reacted with singlet oxygen to >99% consumption within a 14-hour period. These results suggest that the aminic antioxidant tested could primarily be a chemical quencher of singlet oxygen, which would contribute to the substantial quenching that was seen with the compound over the other two Lubrizol samples.

However, if the aminic antioxidant does in fact only react as a chemical quencher and does not further react to reform the initial compound then this could hinder its usefulness over longer periods of use. Further testing would be required over significantly longer periods of time, in the absence of the actinometer, to determine whether there is in fact a reaction chemical reaction occurring between the aminic antioxidant and singlet oxygen, as well as testing for products using chromatography to determine if there are any further reactions occurring.

Table 25 - Comparison of Quenching Constants for Each Sensitizer

	Sensitizer	
	Methylene Blue	**Zinc Phthalocyanine**
Calculated k_q	2.54×10^7 $dm^3mol^{-1}s^{-1}$	1.28×10^7 $dm^3mol^{-1}s^{-1}$

Since there were issues with testing the sulfurized olefin using methylene blue as the sensitizer, as discussed in chapter 6, a different sensitizer had to be found which would provide similar enough results to be comparable with the ones obtained using methylene blue. The table above shows the overall results for the testing of the aminic antioxidant with the two different sensitizers.

While there is a slight decrease in the calculated singlet oxygen quenching rate constant when using zinc phthalocyanine as the sensitizer, both values are still within the scope of the error. Since there appears to be no significant difference between the results obtained for the singlet oxygen quenching rate constant of the aminic antioxidant when using zinc phthalocyanine vs. using methylene blue it can be seen that the results obtained for the sulfurized olefin using this sensitizer can confidently be compared to those obtained using methylene blue.

7.1.2. Phenolic

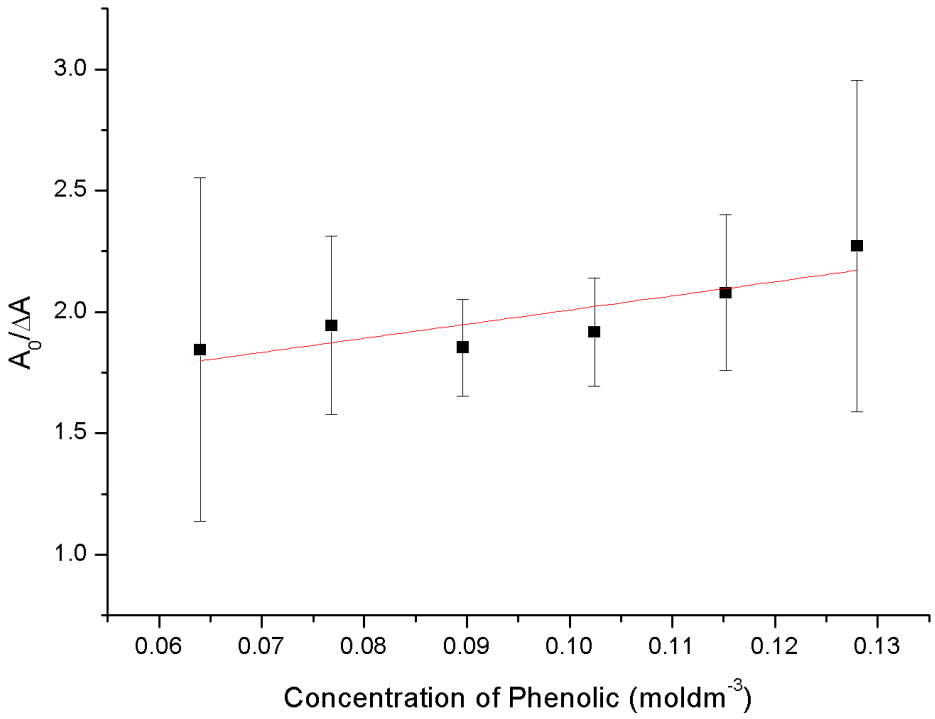


Figure 41 - Phenolic Steady-state (in 1-butanol)

Table 26 - Phenolic Steady-state (in 1-butanol)

Adjusted R-Square	0.65406
	Value
Intercept	1.42582
Slope	5.82278 dm^3mol^{-1}
Calculated k_q	2.31 x 10^5 $dm^3mol^{-1}s^{-1}$

From the results seen in figure 41, it cannot be said with any certainty that there is significant singlet oxygen quenching occurring due to the phenolic antioxidant under the conditions tested. This is due to the high deviations within the data, most clearly noticeable in the lowest and highest concentration data sets. This outcome is somewhat unexpected as the phenolic antioxidant has similarities in its structure to that of α-tocopherol, which is known to be a strong singlet oxygen quencher.

While it was expected that the aminic sample would show the highest quenching of the three Lubrizol samples, the value calculated for the phenolic sample is significantly lower.

7.1.3. Sulfurized Olefin

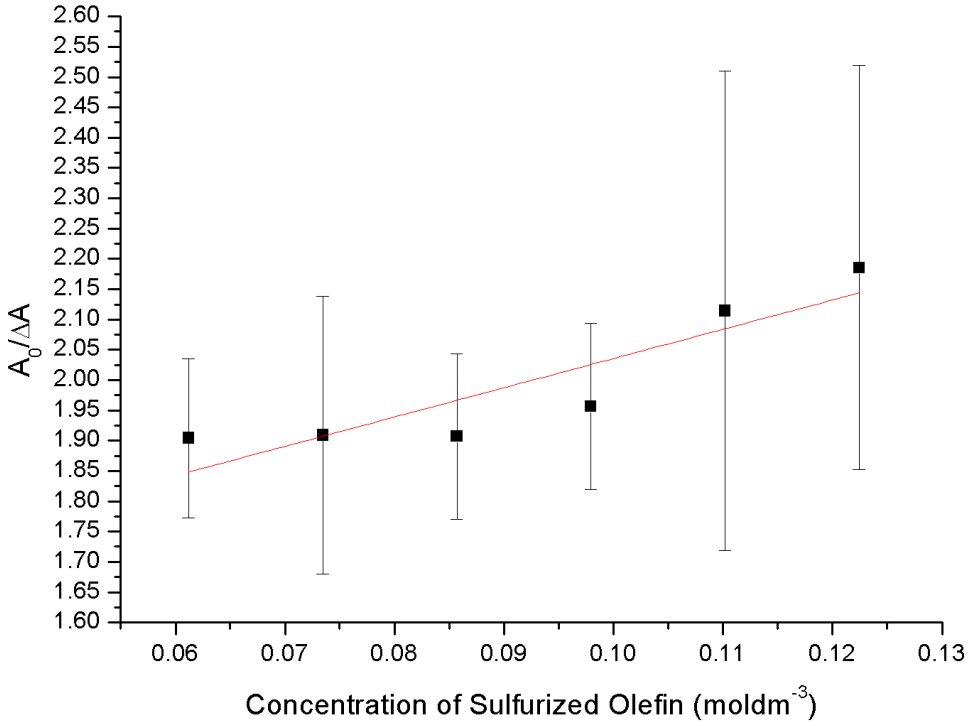


Figure 42 - Sulfurized Olefin Steady-state (in 1-butanol)

Table 27 - Sulfurized Olefin Steady-state (in 1-butanol)

Adjusted R-Square	0.76736
	Value
Intercept	1.55279
Slope	4.82799 dm^3mol^{-1}
Calculated k_q	1.94 x 10^5 $dm^3mol^{-1}s^{-1}$

The results obtained for the sulfurized olefin show some high standard deviations within the data set, especially at the higher concentrations. However, a slight positive trend can still be discerned from the data acquired. This would have to be retested whilst trying to minimise the possible errors to see if this is in fact the case.

One significant complication faced when analysing the Lubrizol antioxidants is that each of the samples supplied are a mixture of products from the synthesis process, with the sulfurized olefin in particular being known to be the least pure of the antioxidants provided, as discussed back in chapter 4. Therefore, it is possible that side reactions from other products within the mixture could be competing with the quenching pathway and thus contributing to the fluctuations and larger standard deviation seen within the results.

7.1.4. Squalene

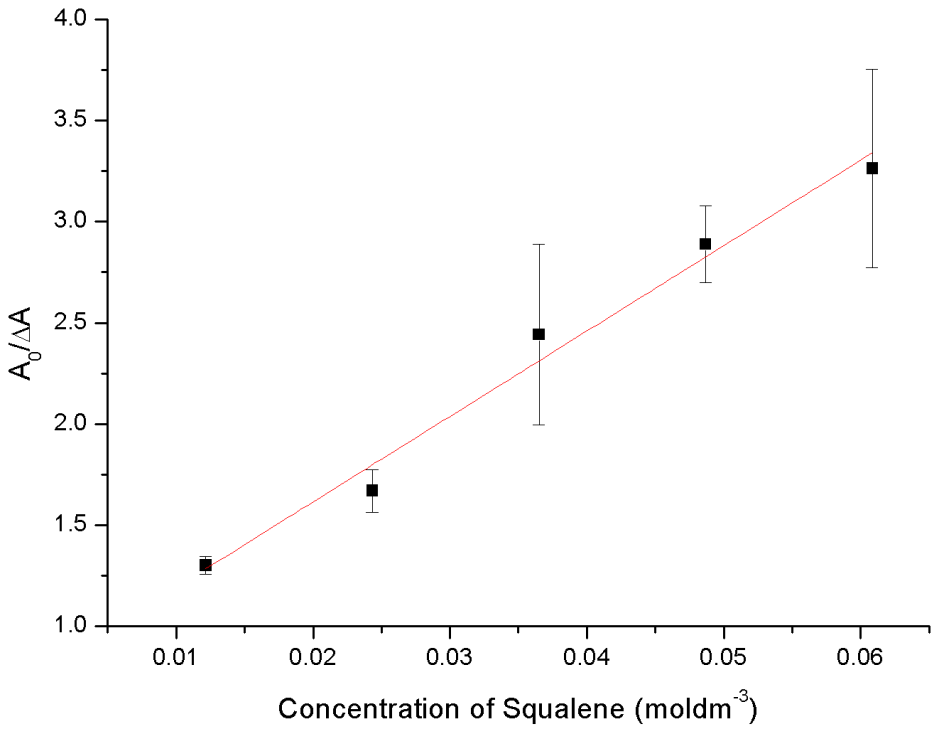


Figure 43 - Squalene Steady-state (in 1-butanol)

Table 28 - Squalene Steady-state (in 1-butanol)

Adjusted R-Square	0.97829
	Value
Intercept	0.77077
Slope	42.23238 dm^3mol^{-1}
Calculated k_q	3.18 x 10^6 $dm^3mol^{-1}s^{-1}$

The values obtained for squalene showed good correlation with a high R-square value when calculating the fit, suggesting that the values obtained are at least precise. The similarity of the results obtained to those found within the literature also confirm their accuracy[32].

With these results, it can be seen that there is a strong quenching effect due to the presence of squalene, thus suggesting that it would be a strong potential antioxidant for use with formulations.

7.1.5. Overall Conclusions

From the information gathered over the course of the research it became clear that the methods used to obtain the singlet oxygen quenching constants were giving results similar to those previously published by other researchers, giving confidence that the results obtained here were reliable, in terms of the method used.

It was expected that α-tocopherol would give the highest value for its quenching constant and that was confirmed by the results shown. Interestingly the aminic antioxidant also proved to be a significant singlet oxygen quencher, showing values slightly less than those shown for α-tocopherol but higher than the other potential quenchers tested. This also correlates with information from Lubrizol than stated the aminic antioxidant showed the highest antioxidant ability out of the three compounds provided from their lubricant additive formulations.

From the results seen here it seems that of the antioxidants provided by Lubrizol the ‘radical scavengers’, the aminic and the phenolic, are more efficient at quenching singlet oxygen than the ‘peroxide scavenger’ the sulfurized olefin.

Information provided previously from Lubrizol indicated that within additive formulations the aminic antioxidant that was provided for testing was known to be the most efficient antioxidant of the three. Meanwhile the sulfurized olefin was not known to be as significant an antioxidant since it works within the formulations in a different way.

Out of the three Lubrizol antioxidants the order of their singlet oxygen quenching capacity was shown to be the aminic, the phenolic then the sulfurized olefin. This fits with information provided by Lubrizol.

7.2. Near-IR Singlet Oxygen Luminescence Measurements

7.2.1. α-Tocopherol

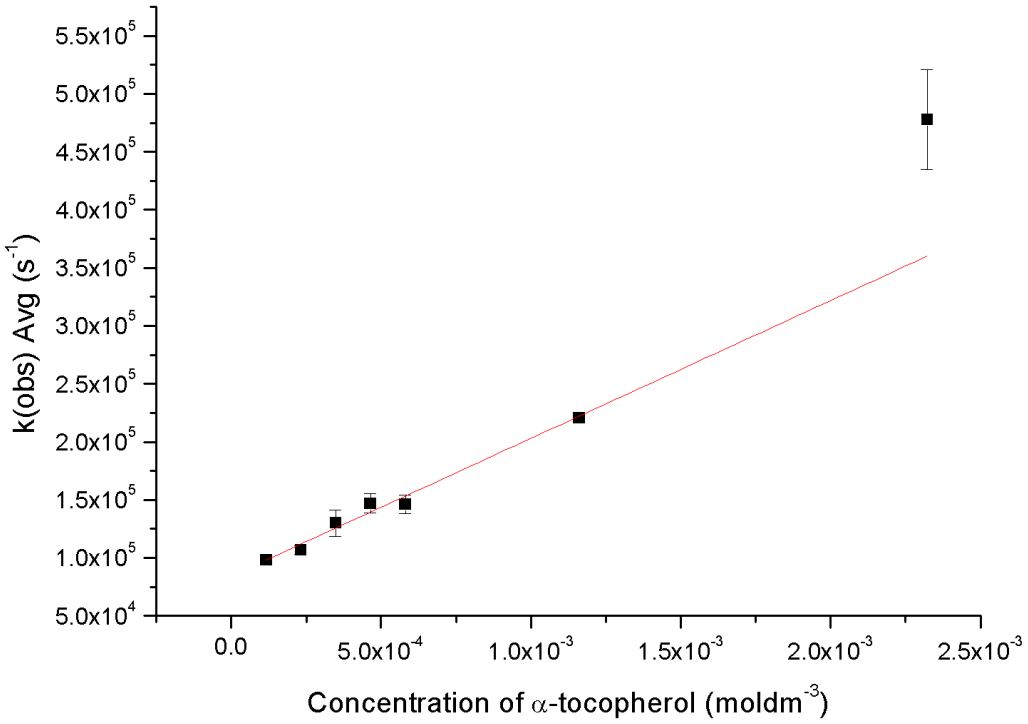


Figure 44 - Alpha-tocopherol Lifetime Data (in 1-butanol)

Table 29 - Alpha-tocopherol Lifetime Data (in 1-butanol)

Adjusted R-Square	0.98558
	Value
Intercept	84323.90025
Slope	1.1876×10^8 $dm^3mol^{-1}s^{-1}$
Calculated k_q	1.19×10^8 $dm^3mol^{-1}s^{-1}$

There is a strong positive correlation within the data obtained. However, the highest concentration does deviate from the linearity of the plot, suggesting the possibility of non-linearity increasing in the singlet oxygen quenching at higher concentrations. To confirm this data for extra concentrations between the two highest concentrations would need to be tested.

Overall from the data gathered there appears to be little difference between the values for k_q obtained using the steady-state and lifetime methods. As such the value obtain from the lifetime measurements is also concurrent with the literature values for α-tocopherol in ethanol.

7.2.2. Aminic

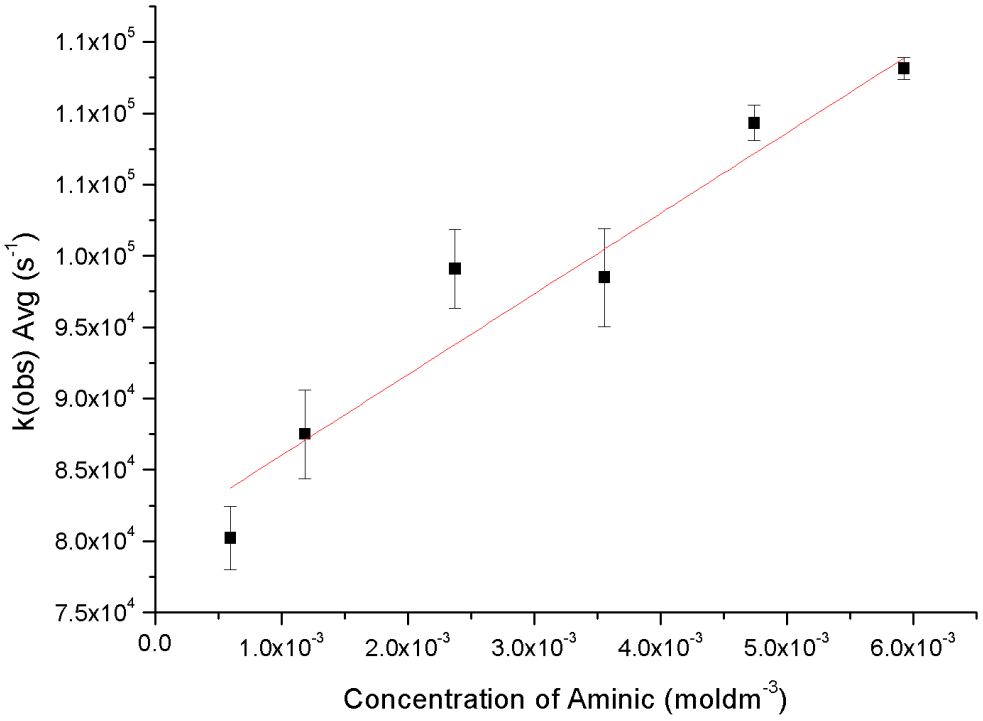


Figure 45 - Aminic Lifetime Data (in 1-butanol)

Table 30 - Aminic Lifetime Data (in 1-butanol)

Adjusted R-Square	0.95117
	Value
Intercept	80398.34369
Slope	5.64835×10^6 $dm^3mol^{-1}s^{-1}$
Calculated k_q	5.65×10^6 $dm^3mol^{-1}s^{-1}$

The plot of the data for Lubrizol's aminic sample shows a linear correlation between singlet oxygen quenching rate and concentration. Interestingly the value for k_q obtained using the lifetime measurements is approximately an order of magnitude lower than that found using the steady-state measurements.

This difference in the values obtained is most likely due to the possibility of alternative reactions that could be occurring and affecting the absorbance at the selected wavelength. Given the longer time frame across the steady-state measurements there is a larger window of opportunity for other reactions and by-product build up to occur. If there is in fact by-products forming within the reaction mixture then it is possible that these products could have absorptions which overlap with that of the 9,10-anthracene actinometer and thus effecting the observed overall change in absorption. It might be possible to compensate for this by utilising a different acceptor that absorbs at a different wavelength, this will be discussed later in chapter 11.

7.2.3. Phenolic

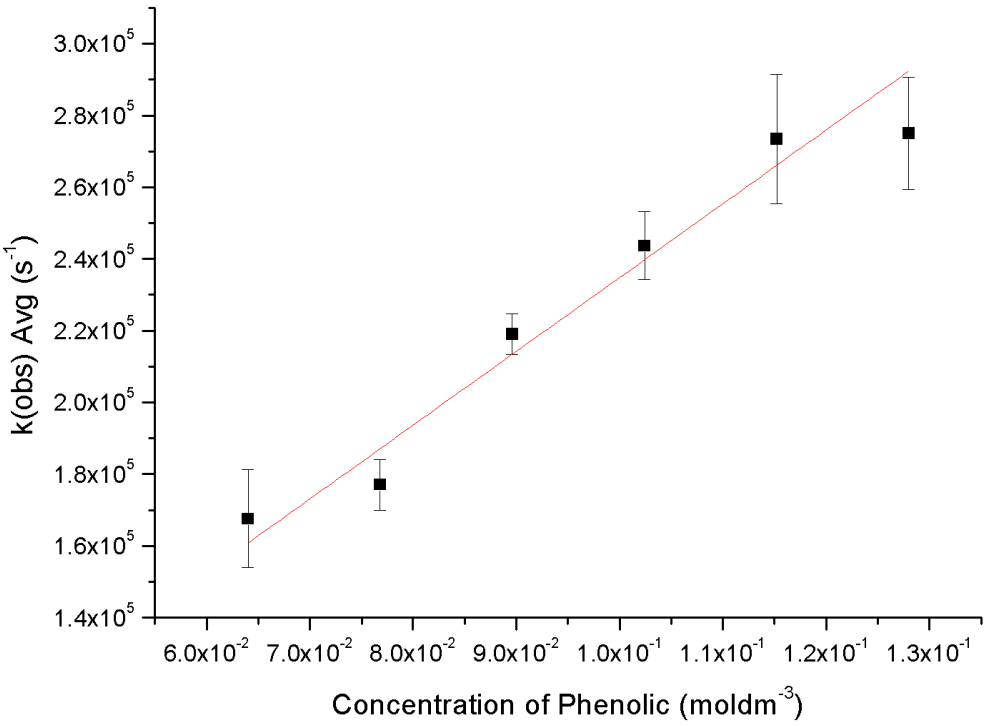


Figure 46 - Phenolic Lifetime Data (in 1-butanol)

Table 31 - Phenolic Lifetime Data (in 1-butanol)

Adjusted R-Square	0.92052
	Value
Intercept	29105.48343
Slope	2.05745×10^6 $dm^3mol^{-1}s^{-1}$
Calculated k_q	2.06×10^6 $dm^3mol^{-1}s^{-1}$

The plot of this data does show a convincing linear, positive correlation between the quenching rate constant and concentration.

Overall the value for k_q calculated from the data gathered using the lifetime measurements is approximately an order of magnitude higher than that calculated using the steady-state measurements. As was stated earlier with the aminic results, it is possible that there are some interactions occurring during the steady-state measurements that are affecting the results in a significant enough way that can be seen in the difference between the calculated k_q values.

7.2.4. Sulfurized Olefin

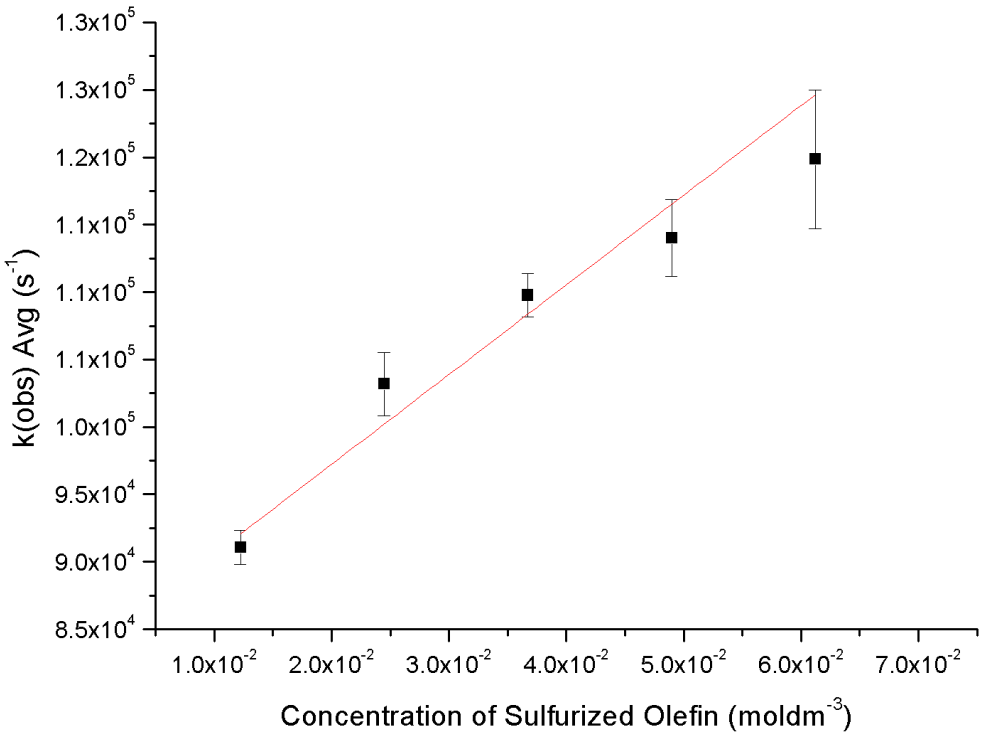


Figure 47 - Sulfurized Olefin Lifetime Data (in 1-butanol)

Table 32 - Sulfurized Olefin Lifetime Data (in 1-butanol)

Adjusted R-Square	0.95048
	Value
Intercept	83947.76613
Slope	665030.95467 $dm^3mol^{-1}s^{-1}$
Calculated k_q	$6.65x10^5$ $dm^3mol^{-1}s^{-1}$

Unlike with the steady-state data obtained for the sulfurized olefin, the singlet oxygen lifetime data shows a vastly clearer positive trend with significantly less error associated with the data.

The value obtained for k_q from this data is higher than that obtained from the steady-state data, although still within the same order of magnitude. This lends more strength to the reliability of the steady-state method, at least for this antioxidant.

7.2.5. Squalene

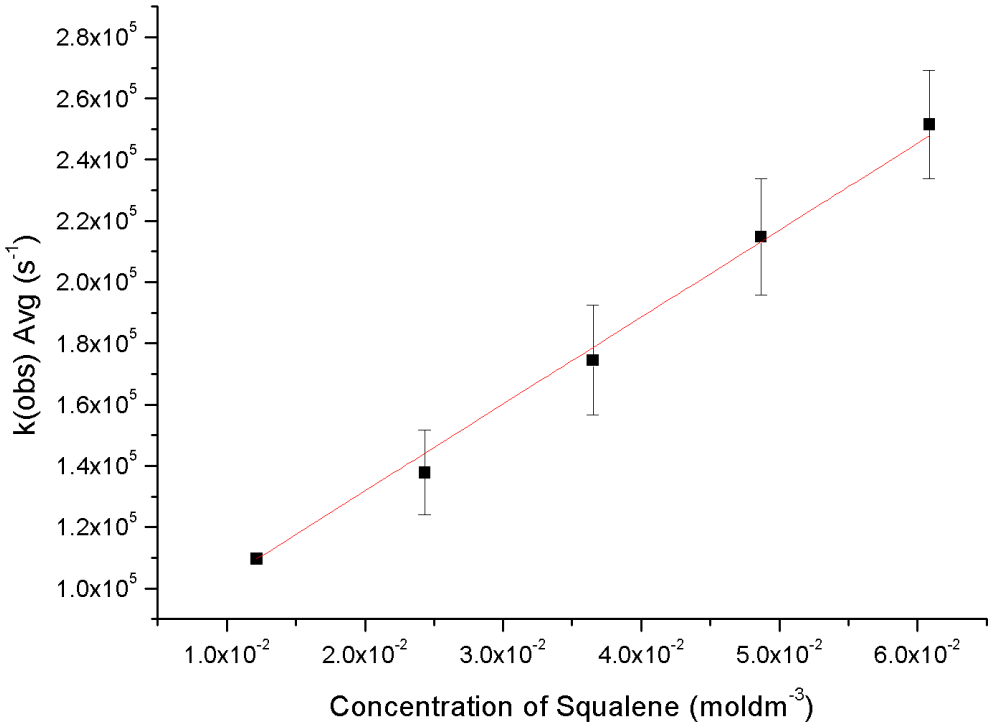


Figure 48 - Squalene Lifetime Data (in 1-butanol)

Table 33 - Squalene Lifetime Data (in 1-butanol)

Adjusted R-Square	0.99612
	Value
Intercept	75088.64402
Slope	2.83728×10^6 $dm^3mol^{-1}s^{-1}$
Calculated k_q	2.84×10^6 $dm^3mol^{-1}s^{-1}$

There is very clear and strong positive correlation within the squalene lifetime data and although there is still error within the data the fit is confidently precise. The calculated k_q value is similar to that obtained using the steady-state measurements, albeit both values being slightly lower than that found in the literature for testing in ethanol.

7.2.6. Overall Conclusions

Overall it appears that the data gathered using the singlet oxygen lifetime measurements tended to show clearer trends within the data as well as having overall less error associated with the data than the steady-state measurements. This stronger reliability of the results obtained using this method, coupled with the vastly greater speed at which these measurements can be obtained, suggests this method is superior to the steady-state method, in terms of precision.

That being said, the significantly higher cost associated with the system required to obtain the lifetime measurements, especially the specific hardware requirements, make this system less optimal for small scale testing. However, this technique could be very beneficial for initial testing of new compounds, or variations of a compound, where larger quantities of samples and speed of gathering results would be more important.

It can also be noted that the singlet oxygen lifetime measurements give less opportunity to test other factors that could influence the quenching of singlet oxygen, such as temperature or detecting other reactions, including attempting to discern the possibility of chemical quenching. As will be discussed later the steady-state method is able to be utilised to test for a wider range of influences due to the systems simplified nature and therefore its adaptiveness.

Interestingly, it can also be noted that the values for k_q calculated using the steady-state method for the two non-Lubrizol antioxidants, squalene and α-tocopherol, were closer to those found in the literature[32] than the values calculated using the singlet oxygen lifetime method. This

lends credence to the steady-state method as being able to be utilised to obtain accurate quenching constants, at least in pure systems.

However, it must also be taken into consideration that the literature values discussed here are for tests conducted in ethanol and not 1-butanol like the samples were tested in for this report. As well as this it can also be seen that there is not a significant difference between the values obtained via the two different methods, thus validating both methods as being able to obtained accurate results.

7.3. 1-Butanol vs Hexadecane

7.3.1. Aminic

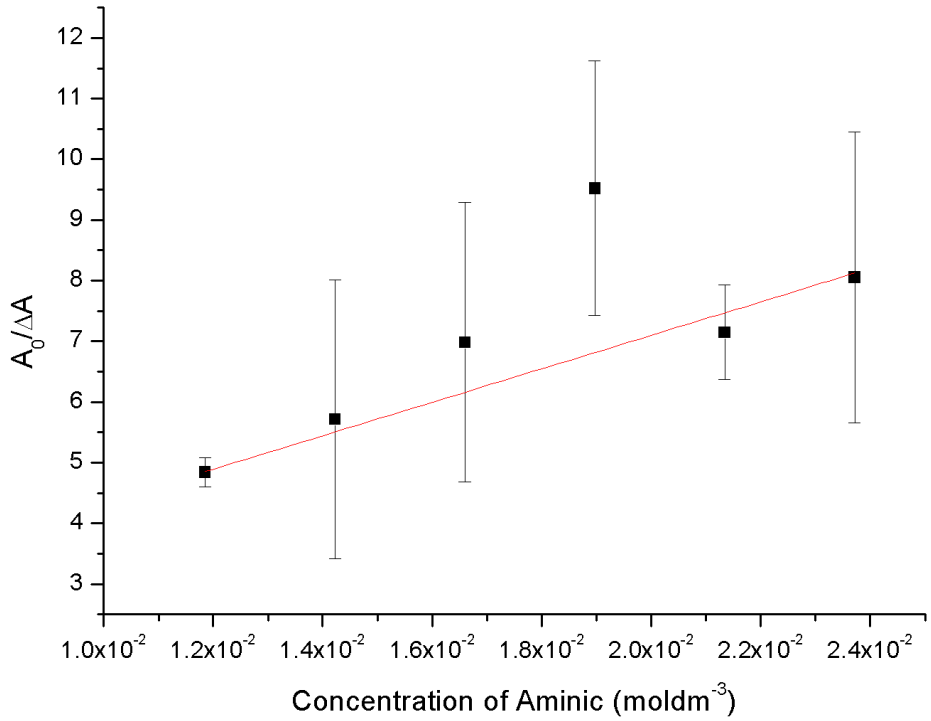


Figure 49 - Aminic Steady-state (in Hexadecane)

Table 34 - Aminic Steady-state (Hexadecane with 1-butanol for Comparison)

Adjusted R-Square	0.83297
	Value
Intercept	1.58212
Slope	275.82331 dm^3mol^{-1}
Calculated k_q (hexadecane)	1.03 x 10^7 $dm^3mol^{-1}s^{-1}$
Calculated k_q (1-butanol)	2.54 x 10^7 $dm^3mol^{-1}s^{-1}$

While there is one apparent value diverging from the general fit, even accounting for the errors, there is still a clear positive trend in the data. Observing the values obtained during the steady-state analysis in 1-butanol and hexadecane, the values appear to be similar enough to suggest little to no solvent effect on the aminic antioxidant's capacity for singlet oxygen quenching when transferring between a polar and non-polar solvent.

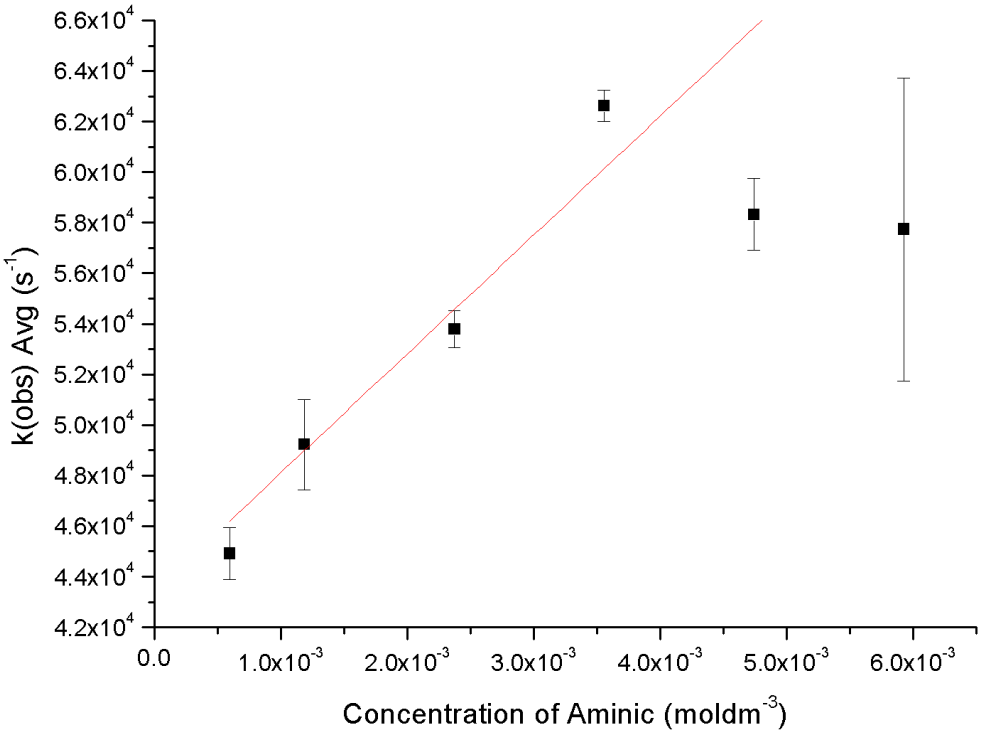


Figure 50 - Aminic Lifetime (in Hexadecane)

Table 35 - Aminic Lifetime (Hexadecane with 1-butanol for Comparison)

Adjusted R-Square	0.75275
	Value
Intercept	43426.01
Slope	4.70×10^6 $dm^3mol^{-1}s^{-1}$
Calculated k_q (hexadecane)	4.70×10^6 $dm^3mol^{-1}s^{-1}$
Calculated k_q (1-butanol)	5.65×10^6 $dm^3mol^{-1}s^{-1}$

With the lifetime data there is some divergence at the higher concentrations; however, as with the steady-state hexadecane data, there is still a clear positive trend with increasing concentration. These measurements were taken at concentrations less than a tenth of those obtained in the steady-state measurements. As with the steady-state data, the same comparison can be made with the lifetime data that due to the similarities in the results obtained in both 1-butanol and hexadecane it can be concluded that there is little to no solvent effect influencing the quenching effect of the aminic antioxidant.

This effect was also seen by Lemp *et al*.[98] who studied solvent effects on the reaction between singlet oxygen and a number of cyclic and acyclic α-diimines. In their research they found that the 5,6-disubstituted cyclic α-diimines tested reacted in a comparable way, with higher rate constants found in tests with polar solvents. However, they also found that there as little to no solvent effect for the 1,4-disubstituted acyclic α-diimines tested.

7.3.2. Phenolic

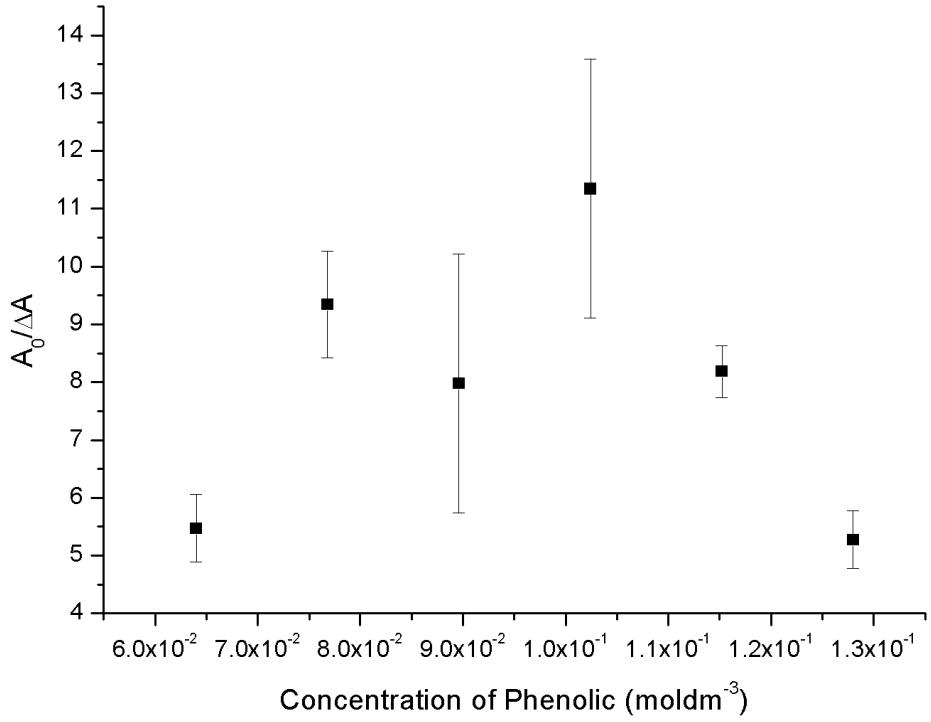


Figure 51 - Phenolic Steady-state (in Hexadecane)

With the data gathered using the steady-state method there was no clear enough trend to justify calculating the singlet oxygen quenching constant. As such it could be suggested from this data set that there is no significant quenching on singlet oxygen occurring from the phenolic sample in hexadecane over the concentration range used. It is possible that there are some very significant solvent effects occurring, mostly likely due to the change in polarity.

There are some similarities in the structures of the phenolic sample and α-tocopherol, both of which have shown reduced singlet oxygen quenching in the non-polar solvent. This is strongly suggesting that both of these compounds quench singlet oxygen using a charge-transfer mechanism.

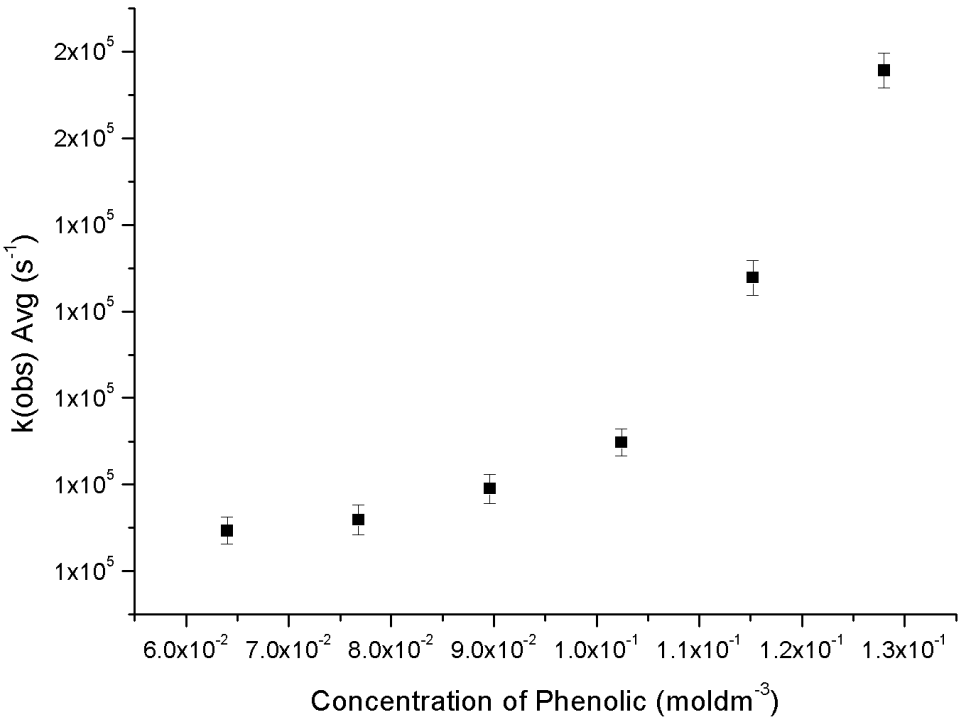


Figure 52 - Phenolic Lifetime (in Hexadecane)

Table 36 - Phenolic Lifetime (Hexadecane with 1-butanol for Comparison)

Adjusted R-Square	0.72845
	Value
Intercept	50930.33
Slope	7.23×10^5 $dm^3mol^{-1}s^{-1}$
Calculated k_q (hexadecane)	7.23×10^5 $dm^3mol^{-1}s^{-1}$
Calculated k_q (1-butanol)	2.06×10^6 $dm^3mol^{-1}s^{-1}$

From the plots of the data there is a very clear and significant difference between what was observed using the steady-state method to what has been observed using the lifetime measurements. From the lifetime measurements it can be seen that singlet oxygen quenching by the phenolic sample is indeed still occurring. Due to the curvature seen in the plot over the full concentration range the quenching constant had to be calculated across the lower concentrations only; from 6.40×10^{-2} $moldm^{-3}$ to 1.02×10^{-1} $moldm^{-3}$.

However, a curved trend can be seen in the data over this concentration range rather than a linear trend. It is possible that at the lower concentrations there is no significant quenching

occurring, but that after a certain point there is enough phenolic present in the system to show signs of quenching. This is supported by the fact that the calculated rate constant over this concentration range is significantly lower than the one calculated from the lifetime data in 1-butanol.

A possible explanation for this occurrence could be the formation of an aggregate between a number of phenolic molecules within a non-polar solvent, where the aggregate is more readily able to quench singlet oxygen over a single molecule. This could also account for the curvature in the data since higher concentrations of the singular molecule would lead a higher probability of collisions and therefore a higher probability of aggregate formation.

7.3.3. Sulfurized Olefin

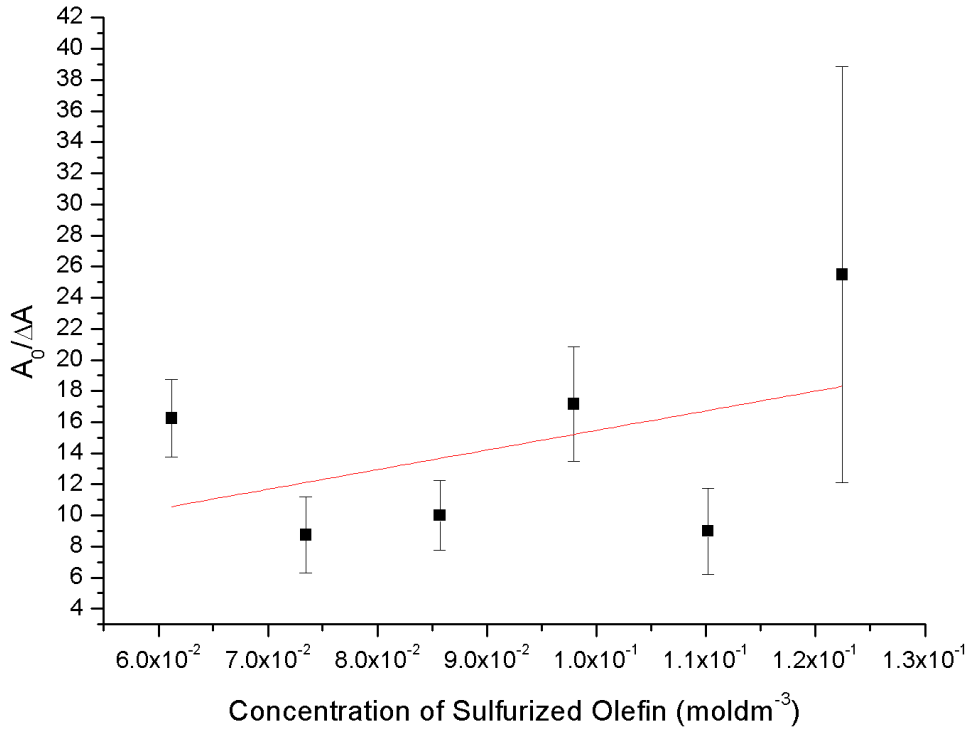


Figure 53 - Sulfurized Olefin Steady-state (in Hexadecane)

Table 37 - Sulfurized Olefin Steady-state (Hexadecane with 1-butanol for Comparison)

Adjusted R-Square	0.83297
	Value
Intercept	1.58212
Slope	275.82331 dm^3mol^{-1}
Calculated k_q (hexadecane)	2.58 x 10^6 $dm^3mol^{-1}s^{-1}$
Calculated k_q (1-butanol)	1.94 x 10^5 $dm^3mol^{-1}s^{-1}$

The data gathered in hexadecane for the sulfurized olefin is troublesome in that it appears to be rather scattered around the fitting plot. While it could still be suggested that there is, at least, a slight positive trend this could suggest that there is indeed some solvent effect at play here.

This is most likely due to the change in polarity between the two solvents, which if the quenching is occurring at least partially via a charge transfer mechanism could interfere with the process.

As with the 1-butanol results, it is possible that side reactions from other products within the mixture competing with the quenching pathway could be contributing to the fluctuations seen within the results.

It could also be suggested that if there is a notable change in the mixture, or how certain products within the mixture react within the hexadecane medium, then the observed quenching could change. Therefore, it would be of interest to separate out the components of the mixture for testing separately to see which particular product is providing the singlet oxygen quenching that has been seen so far. The potential implications of which will be discussed more with the other further work in chapter 11.

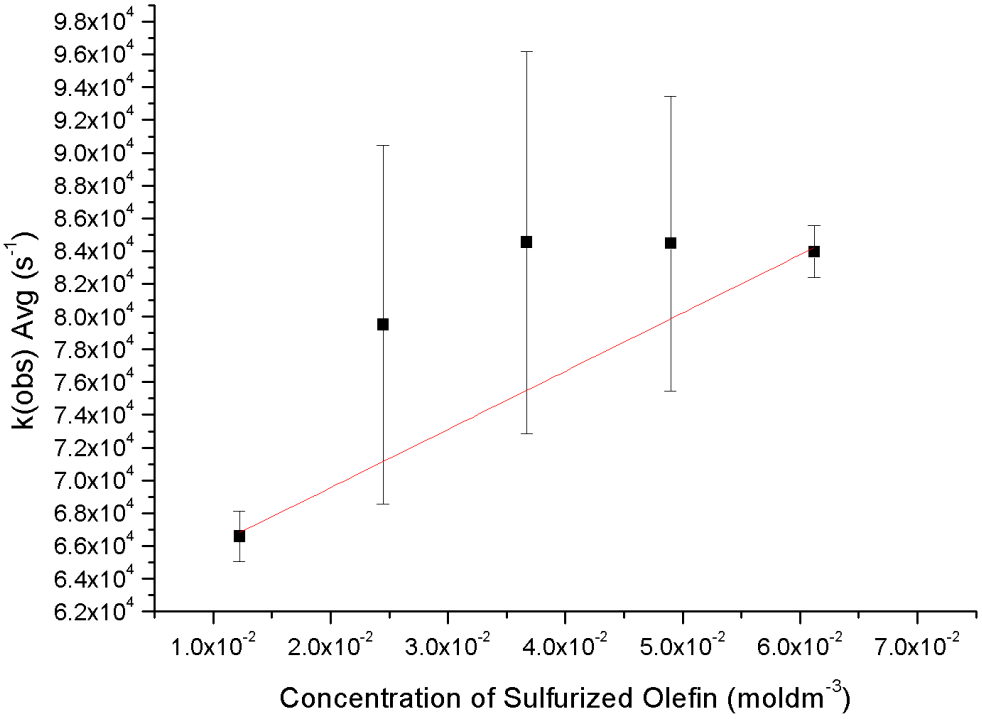


Figure 54 - Sulfurized Olefin Lifetime (in Hexadecane)

Table 38 - Sulfurized Olefin Lifetime (Hexadecane with 1-butanol for Comparison)

Adjusted R-Square	0.9689
	Value
Intercept	62458.8001
Slope	3.55 x10^5 $dm^3mol^{-1}s^{-1}$
Calculated k_q (hexadecane)	3.55 x10^5 $dm^3mol^{-1}s^{-1}$
Calculated k_q (1-butanol)	6.65x10^5 $dm^3mol^{-1}s^{-1}$

7.3.4. Squalene

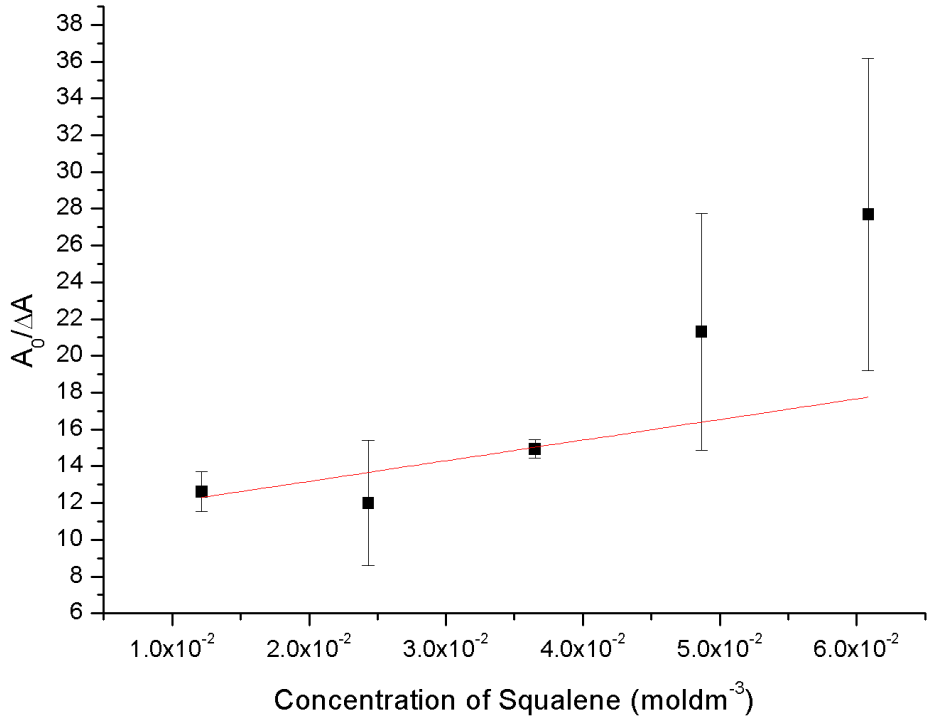


FIGURE 55 - SQUALENE STEADY-STATE (IN HEXADECANE)

Table 39 - Squalene Steady-state (Hexadecane with 1-butanol for Comparison)

Adjusted R-Square	0.60955
	Value
Intercept	10.93682
Slope	112.10551 dm^3mol^{-1}
Calculated k_q (hexadecane)	6.14 x 10^5 $dm^3mol^{-1}s^{-1}$
Calculated k_q (1-butanol)	3.18 x 10^6 $dm^3mol^{-1}s^{-1}$

The data obtained suggests a positive correlation between singlet oxygen quenching and concentration within hexadecane for squalene. However, there appears to be very little change initially. This could suggest that the concentration is too low at these points to show significant quenching, since the later concentrations do show quenching.

It would be of interest to repeat the measurement at the lower concentrations as well as measure higher concentrations of squalene in hexadecane using this method to see if the lower

concentrations were in fact anomalously low and if the positive trend continues at the higher concentrations.

Table 40 - Squalene Steady-state (Hexadecane), Lower Concentrations

Adjusted R-Square	0.82078
	Value
Intercept	1.20172
Slope	377.61041 dm^3mol^{-1}
Calculated k_q	1.88 x 10^7 $dm^3mol^{-1}s^{-1}$

Plotting the data without the lowest concentration gives a significantly stronger positive correlation, as well as a significantly higher calculated k_q value of 1.88 x 10^7 $dm^3mol^{-1}s^{-1}$. This value is in itself significantly higher than that obtained within 1-butanol, suggesting a strong solvent effect between the two.

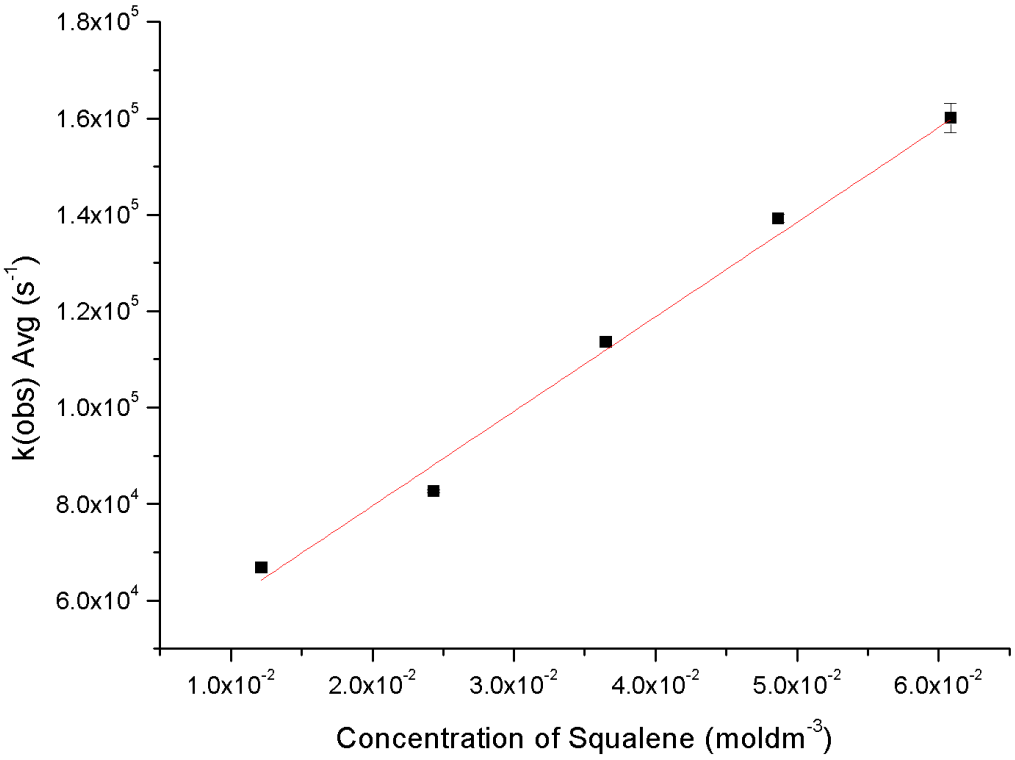


Figure 56 - Squalene Lifetime (in Hexadecane)

Table 41 - Squalene Lifetime (Hexadecane with 1-butanol for Comparison)

Adjusted R-Square	0.96881
	Value
Intercept	40420.9614
Slope	1.96 x 10^6 $dm^3mol^{-1}s^{-1}$
Calculated k_q (hexadecane)	1.96 x 10^6 $dm^3mol^{-1}s^{-1}$
Calculated k_q (1-butanol)	2.84x10^6 $dm^3mol^{-1}s^{-1}$

The data obtained using the lifetime method for squalene in hexadecane shows both a very strong positive correlation between singlet oxygen quenching and antioxidant concentration as well as very little deviation within the data.

However, unlike with the steady-state data, there is no significant difference between the values obtained in 1-butanol and hexadecane using the singlet oxygen lifetime measurements, thus suggesting little to no solvent effect. The differing outcomes between the two methods could potentially be explained by errors within one of the data sets, in this case most probably the steady-state data.

An alternative explanation could be down to a delayed solvent effect occurring. This could be possible since the lifetime measurements take place over a vastly shorter time span, a matter of seconds, than the steady-state measurements, upwards of twenty minutes. The increased duration period used within the steady-state measurements could favour the occurrence of side reactions.

7.3.5. α-Tocopherol

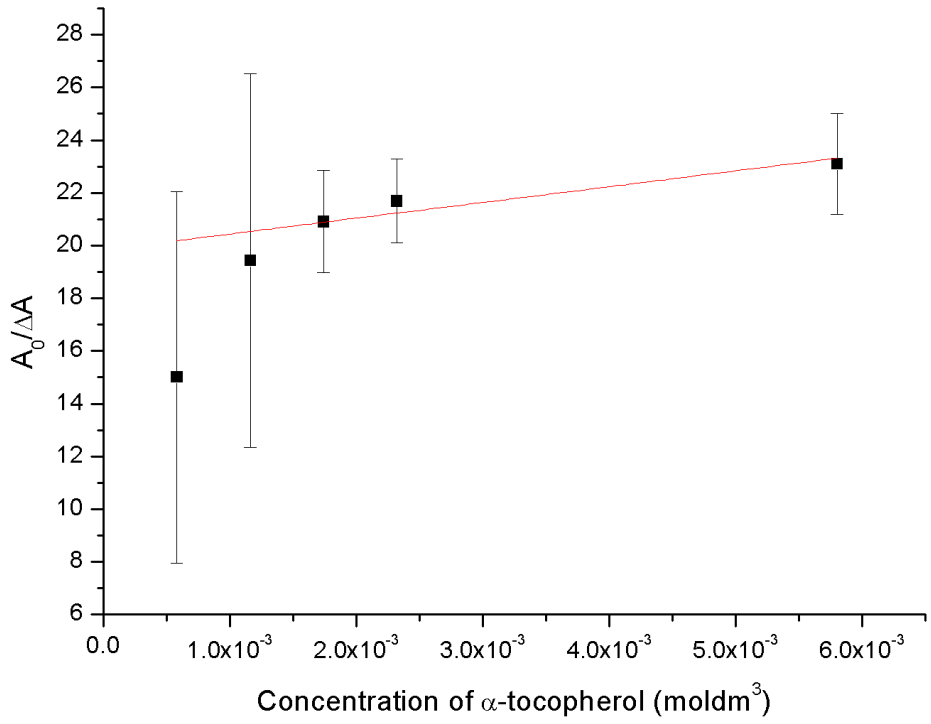


FIGURE 57 - ALPHA-TOCOPHEROL STEADY-STATE (IN HEXADECANE)

Table 42 - Alpha-tocopherol Steady-state (Hexadecane with 1-butanol for Comparison)

Adjusted R-Square	0.48264
	Value
Intercept	19.84375
Slope	597.88512 dm^3mol^{-1}
Calculated k_q (hexadeane)	1.82 x 10^6 $dm^3mol^{-1}s^{-1}$
Calculated k_q (1-butanol)	2.87 x 10^8 $dm^3mol^{-1}s^{-1}$

The plot of the data appears to be plateauing towards the highest concentration within hexadecane. However, the higher proportion of error at the two lowest concentrations could suggest that this may not be the true trend. It would be logical to repeat the measurements at the lowest concentrations whilst attempting to minimise error to confirm if this is the true trend. This could also be achieved by repeating measurements of the highest concentration as well as some measurements of an intermediate concentration between the two highest concentrations previously tested as well as a higher concentration.

For comparison a value for the singlet oxygen quenching rate constant of α-tocopherol in hexadecane of 4.2 x 10^7 $dm^3mol^{-1}s^{-1}$ was found[32]. The calculated value from the steady-state measurements is significantly lower than both the value calculated in 1-butanol was well as that found in the literature.

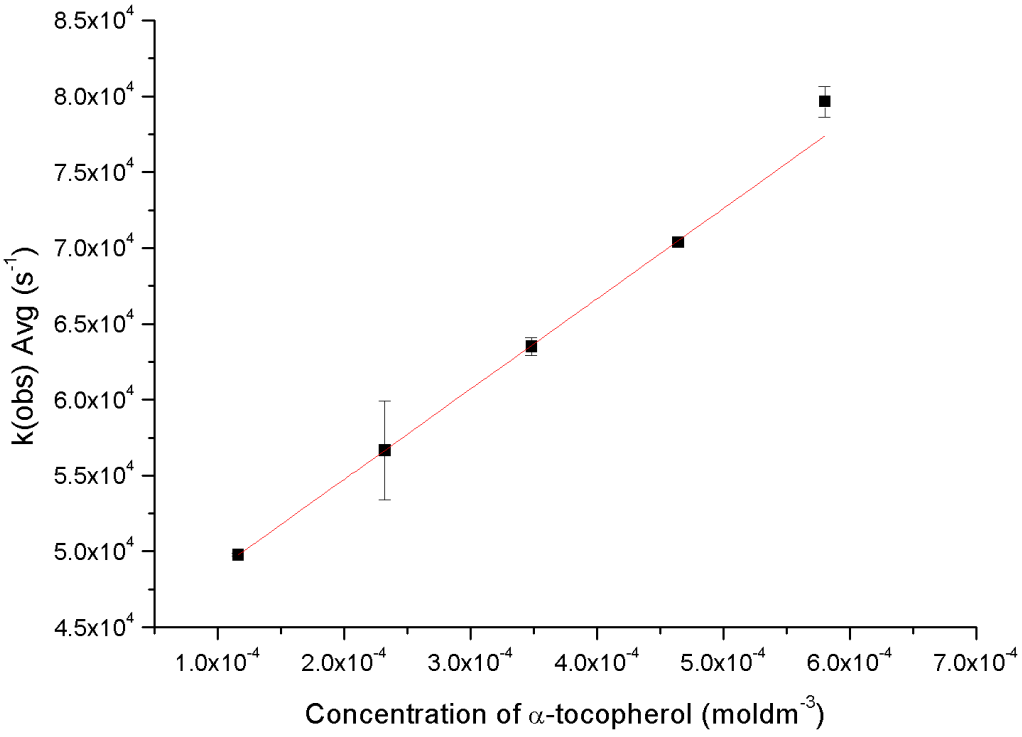


Figure 58 - Alpha-tocopherol Lifetime (Hexadecane)

Table 43 - Alpha-tocopherol Lifetime (Hexadecane with 1-butanol for Comparison)

Adjusted R-Square	0.99916
	Value
Intercept	42863.02
Slope	5.95×10^{7} $dm^3mol^{-1}s^{-1}$
Calculated k_q (hexadecane)	5.95×10^{7} $dm^3mol^{-1}s^{-1}$
Calculated k_q (1-butanol)	1.19×10^{8} $dm^3mol^{-1}s^{-1}$

The plot for the lifetime data is clearly far more linear than that of the steady-state data in hexadecane with less error effecting the results. And while the value obtained is still significantly lower than that obtained from lifetime measurements in 1-butanol by an order of magnitude, the difference between the values is more in keeping with the difference seen in the literature values[32] when changing from a polar alcohol to a non-polar hydrocarbon.

It is clear from all three sources that there is definitely an effect from the solvent medium on the ability of α-tocopherol to quench singlet oxygen. This change is most likely down to the change in polarity between the two solvents since it has been recorded within the literature that α-tocopherol quenches via a charge transfer mechanism. The polarity of the solvent aids in the speed of the charge transfer process, thus increasing the rate of quenching.

7.3.6. Overall Conclusions

There were some interesting effects in changing the solvent from the polar 1-butanol to the non-polar hexadecane. It appeared that the effect was dependant on the antioxidant being tested as well as the method used. For example, significant differences were seen in the singlet oxygen quenching rate constants of squalene and the sulfurized olefin when testing using the steady-state method; however, there was far less of a change seen when testing using the singlet oxygen lifetime method.

These differences are more likely down to differences between the methods. As has been stated previously the longer time frame of the steady-state measurements give more room for side reactions and product formation to occur which could skew the results, albeit whilst giving some insight into the potential outcome of prolonged use of the antioxidants in these systems.

However, the greatest differences in the results between the two methods were seen with the phenolic sample. Using the steady-state method it appeared that there was no significant

quenching occurring. However, under the lifetime method a singlet oxygen quenching rate constant was able to be calculated with little difficulty. Unlike with squalene and sulfurized olefin, the phenolic sample still showed a significant reduction in efficiency in hexadecane even in the lifetime measurements.

Another possible outcome is that the polarity is changing the energy levels of the two encounter complexes that can form during the quenching process. If the hexadecane is lowering the energy requirements for the endo-peroxide encounter complex and increasing the energy requirements for the quenching encounter complex this could also account for fluctuations in the quenching capacity of the antioxidant.

8. Results and Discussion III: Synergies

In this section the results obtained during the testing of various combinations of antioxidants will be discussed. For comparison with the results measured for each combination mixture results for each were also estimated using the results obtained for the individual quenching constants calculated in chapter 7.

These estimations are the approximate values that would be expected should the two antioxidants not be interacting or interfering with one another in the process of quenching. Therefore, any significant deviations from these values would suggest that there are other processes occurring within the mixture that are having a direct impact on the antioxidants quenching efficiency, be it in a positive or negative fashion.

To obtain the plots seen throughout this chapter the initial rate of disappearance of 9,10-dimethylanthracene, in $moldm^{-3}$, was calculated from the slope of the plot of concentration, calculated from the absorbance values at 378nm vs time. The initial rate was used as opposed to the overall rate for the duration of the tests to avoid issues arising from the absorbance values for the 9,10-dimethylanthracene being too low to discern changes after prolonged exposure. This was then either plotted against the relative ratios of the various antioxidants, for the first method, or the concentrations of the various antioxidants, for the second method.

There were a couple of reasons for choosing to use the rate of 9,10-dimethylanthracene disappearance rather than the initial absorbance divided by the change in absorbance, $A_0/\Delta A$, which was used to calculated the individual quenching constants in chapter 7. First and most importantly, with the first method the overall concentration of the antioxidant mixture was not being changed, and as such the same calculations that were used for the individual quenching constants were not applicable to this data as it would require a plot of $A_0/\Delta A$ vs concentration.

Secondly plotting the rate of 9,10-dimethylanthracene disappearance against the ratio of the antioxidants gave a far clearer representation of the differences between the estimated and measured values. This is especially so, as a clear comparison can be drawn between the level of quenching occurring and the rate of 9,10-dimethylanthracene disappearance.

Similar plots were also used to analyse the results from the alternative method. However, it became clear that this method might not be as useful for general comparison of the effect of each antioxidant within the mixture, since the changing concentration would cause a change in

the rate constant each without a change in the synergies. However, due to the fact that there was a change in the concentration it was possible in some cases to attempt to calculate quenching constants from the data which could then be compared to the results from chapter 7.

8.1. Initial Method

8.1.1. Aminic and Phenolic

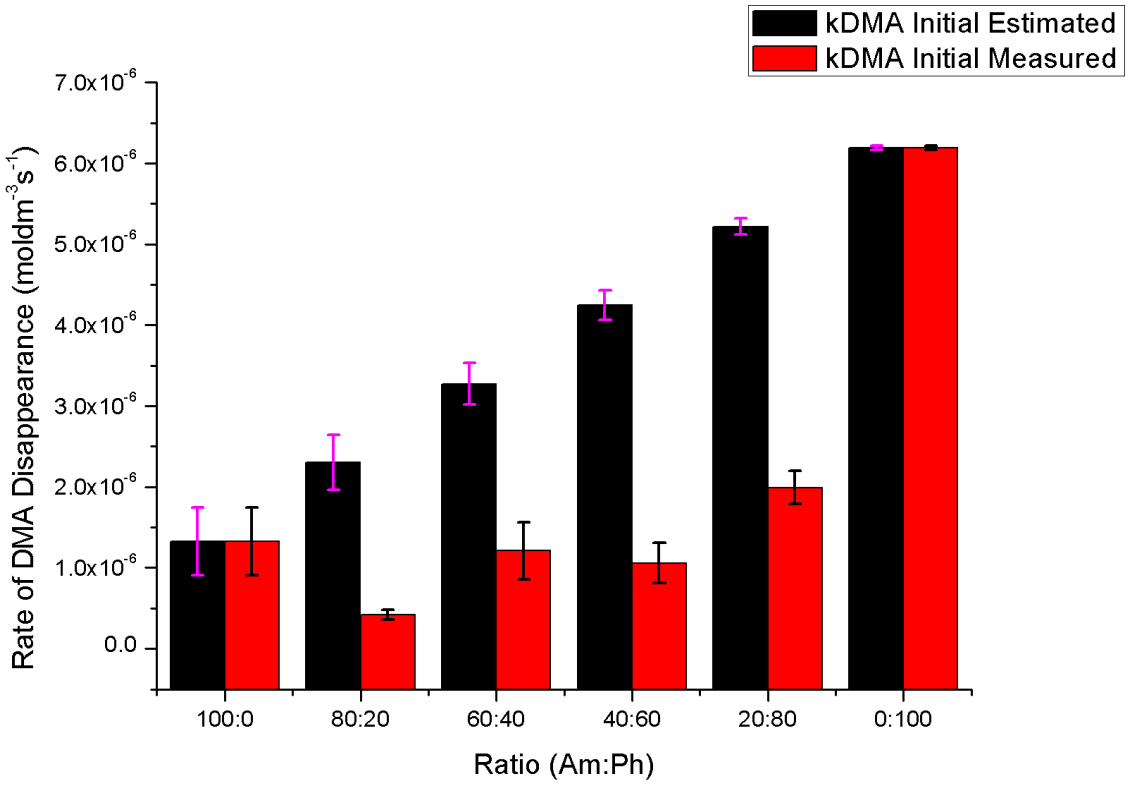


Figure 59 - Rate of DMA Disappearance vs Ratio Aminic to Phenolic

When comparing the initial rates of disappearance of 9,10-dimethylanthracene with the various mixtures of the aminic and phenolic antioxidants present a clear decrease in the rate from what was estimated can be seen in the tests which contained both antioxidants. This strongly suggests that there is indeed a synergistic effect when these two antioxidants are used in conjunction with one another. A fact which was stated before this type of testing started had been seen within results from other in-house tests used by the company.

While an increase in the rate is seen within the estimated results, due to the difference in the two antioxidants' relative singlet oxygen quenching constants, this increase is not as pronounced in the measured results, including deviation from this trend at 40% aminic: 60%

phenolic where the rate does not significantly differ from the rate seen at 60% aminic: 40% phenolic.

The results seen here can be interpreted in a way that can give useful insight and ideas into the development of additive formulations. As stated prior, it can be seen from this data that there is a clear positive effect of the effective singlet oxygen quenching occurring when both antioxidants are used together; however, it can also be seen that a similar effect on the rate that is observed when using solely the aminic antioxidant can be achieved when using the combined mixture.

Depending on the relative costs of the two antioxidants, formulations could be derived that give this level of singlet oxygen quenching whilst also reducing the cost of the materials required to do so. For example, to achieve the same level of singlet oxygen quenching would require a very high concentration of the phenolic antioxidant alone, but by adding a small amount of the aminic antioxidant this could be achieved with a far lower concentration of phenolic.

8.1.2. Aminic and Sulfurized Olefin

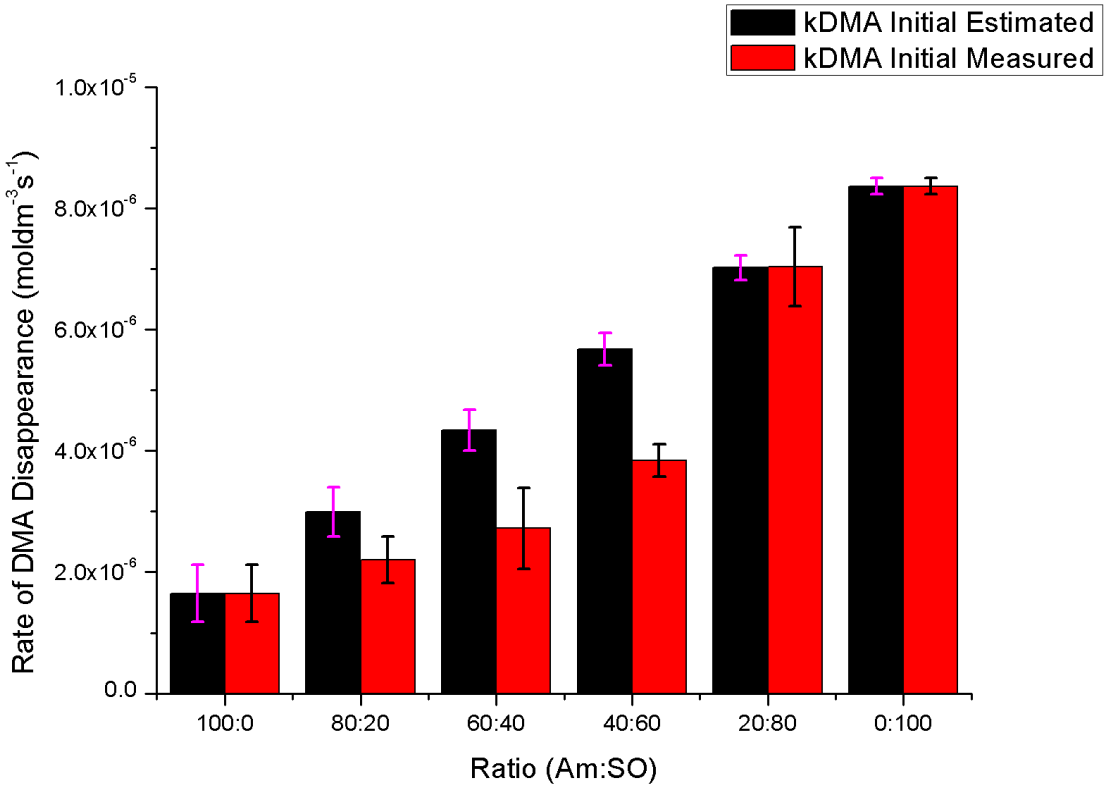


Figure 60 - Rate of DMA Disappearance vs Ratio Aminic to Sulfurized Olefin

Upon initial mixture of the aminic and sulfurized olefin antioxidants it appears that there is little to no deviation from the estimated rates of disappearance of 9,10-dimethylanthracene, as seen at both 80%:20% mixtures; although at 80% aminic: 20% sulfurized olefin is only just so when factoring in the error. However, as the mixtures become more even in the distribution of the concentration between the two, a significant decrease in the rate from the estimated value can also be seen.

The trend of increasing rate with the increasing contribution of the sulfurized olefin to the mixture can be seen in both the estimated and the measured data, although this can be attributed to the fact that the sulfurized olefin has a significantly lower singlet oxygen quenching constant than the aminic antioxidant, as seen in table 23 in chapter 7.

This might suggest that while there is a synergistic effect occurring between these two antioxidants, it is not as pronounced as that which was seen earlier between the aminic and phenolic antioxidants, thus requiring a more balanced formulation to have the greatest effect. However, unlike with the aminic and phenolic mixture, none of the samples containing the aminic and sulfurized olefin mixture showed a decrease of the rate below that seen with the aminic antioxidant alone, a fact which further supports that the synergistic effects seen here are not as pronounced as those seen with an aminic and phenolic mixture.

Since there is an apparent synergy between these two antioxidants, at least at certain points, this information could definitely be utilised, similarly to the information from the aminic and phenolic mixture, to aid in the creation of additive formulations. The knowledge that by using similar ratios of these antioxidants within a formulation should provide increase singlet oxygen quenching from the formulation could vastly improve its performance within the engine system.

8.1.3. Aminic and Squalene

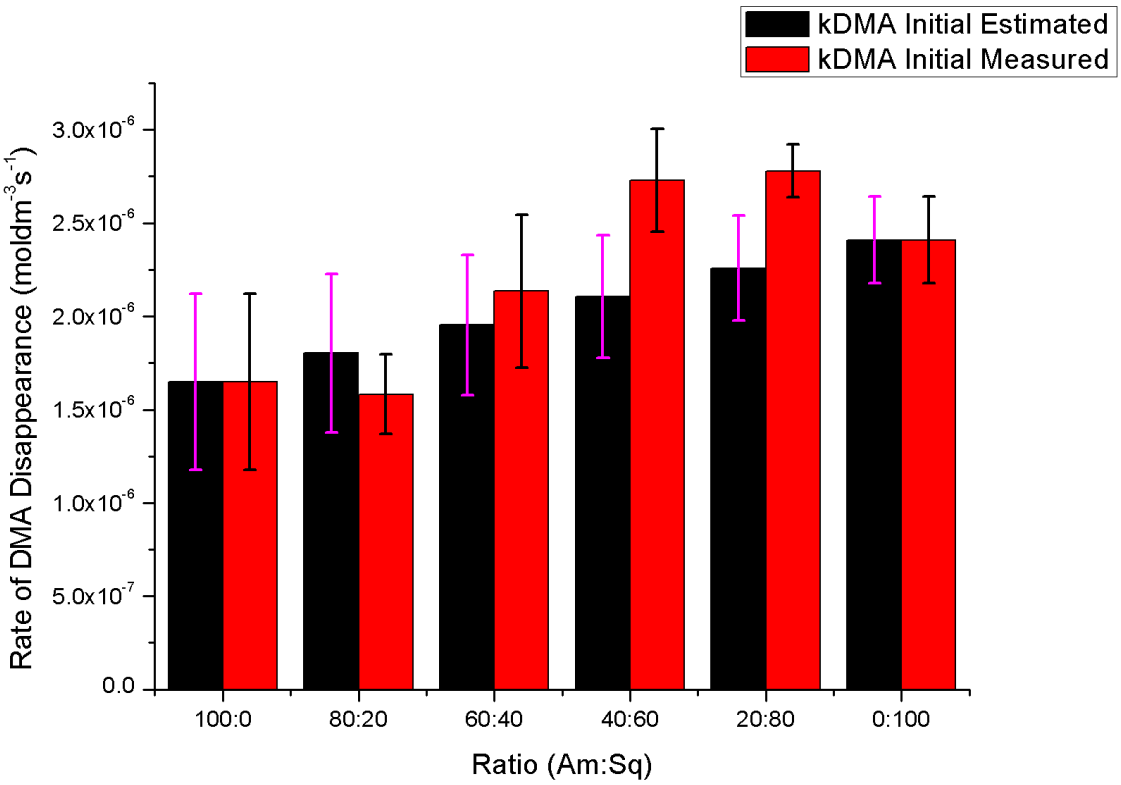


Figure 61 - Rate of DMA Disappearance vs Ratio Aminic to Squalene

Initially, when increasing the ratio of squalene within the antioxidant mixture there appears to be little to no significant deviation from the estimated rates of disappearance for 9,10-dimethylanthrance. However, upon reaching the mixture which contain a greater concentration of squalene than the aminic antioxidant the measured rates can be seen to increase over the estimations.

From the graphical representation in figure 61 it is unclear if the change in the rate measured for the 40% aminic: 60% squalene mixture from the estimated rate is in fact outside of the error and therefore a significant increase, closer inspection of the data itself confirms that it is outside of the error; with $2.43x10^{-6}$ $moldm^{-3}s^{-1}$ being the upper limit of the estimated results while the measured result has a lower limit of $2.45x10^{-6}$ $moldm^{-3}s^{-1}$.

If squalene were to be considered as an additive within any of the Lubrizol formulations it is clear that further testing would be required to discern at what ratio this apparent inhibiting effect begins to have a significant impact on the performance of both antioxidants and whether

these two antioxidants can be utilised together at sufficient concentrations to still be effective enough within a formulation to justify being a part of it.

8.1.4. Phenolic and Sulfurized Olefin

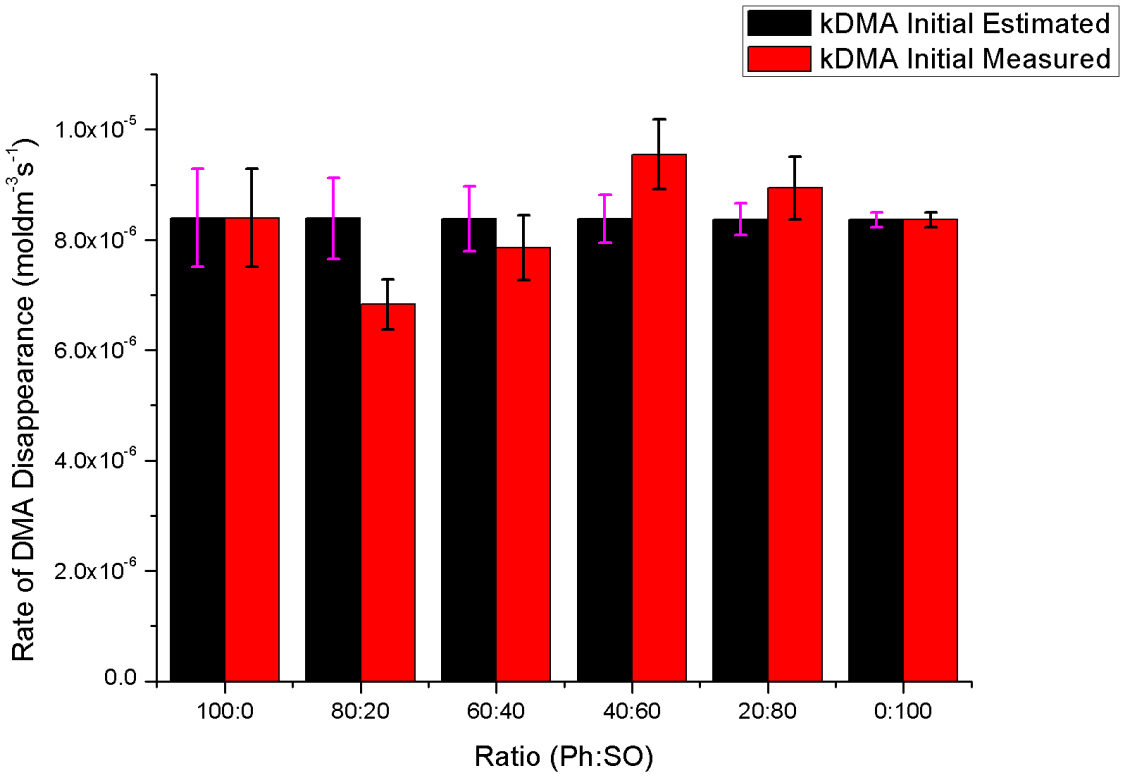


Figure 62 - Rate of DMA Disappearance vs Ratio Phenolic to Sulfurized Olefin

Of all the various ratios that were used within the mixture for testing the only one to show any sign of a synergistic effect occurring between the two antioxidants was at the 80% phenolic: 20% sulfurized olefin combination, where a significant decrease in the initial rate of disappearance of 9,10-dimethylanthracene can be seen.

However, this potential sign of synergistic effects occurring is then not supported by the little to no deviation from the estimated results at the 60:40 and 20:80 combinations. It is further negated by the results at the 40% phenolic: 60% sulfurized olefin combination, where the opposite effect can be seen with a significant increase in the rate of disappearance.

Overall from all of this data it can be suggested that there is no certain sign of a synergistic effect between these two antioxidants; although the same if also true for an inhibitory effect, since only one of the combinations showed signs for either.

Since there is significant interest in knowing for certain of any potential interactions between components within a formulation, to ensure maximum efficiency, it would be a beneficial idea to do further testing with these two antioxidants, perhaps with a greater number of combinations, to confirm that there is no sway one way or the other.

As for the lack of a trend across the various combinations within the estimate results, this is not surprising, since both antioxidants were shown to have similar singlet oxygen quenching constants during the individual testing. As such it would be expected that the relative rate constants of 9,10-dimethylanthracene disappearance for mixtures only involving the antioxidants by themselves would be similar.

8.1.5. Phenolic and Squalene

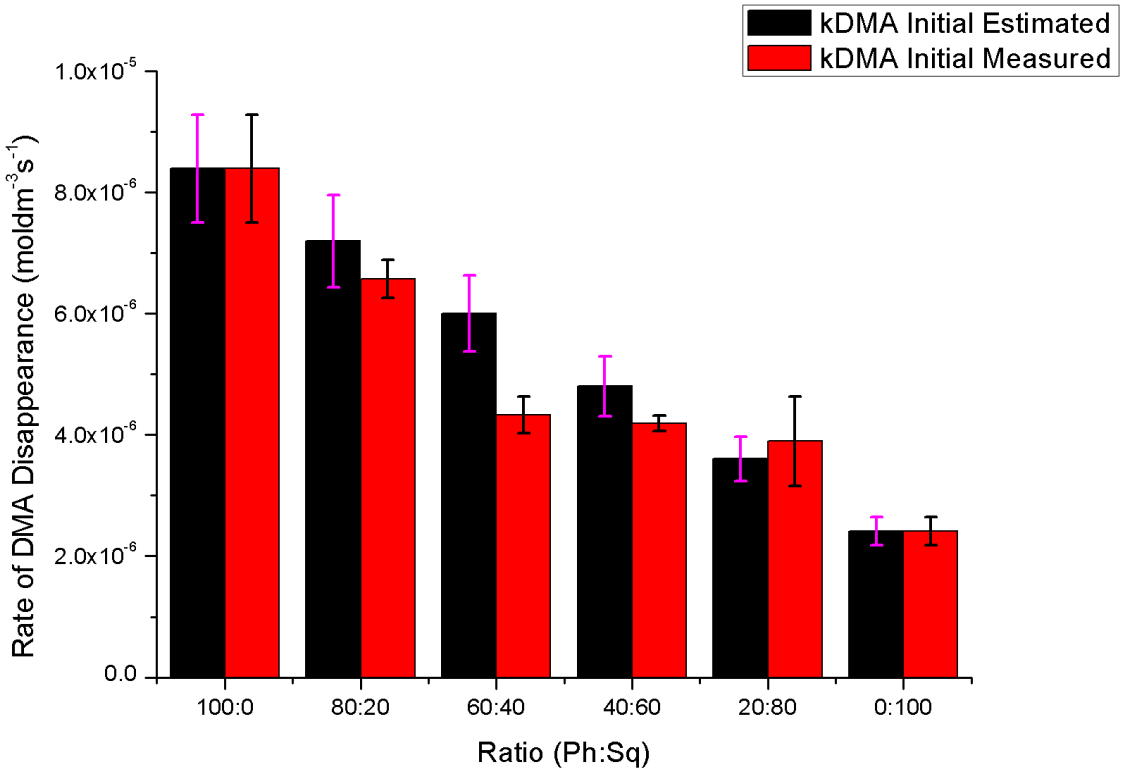


Figure 63 - Rate of DMA Disappearance vs Ratio Phenolic to Squalene

The only measured rate that deviates significantly from those estimated occurs at 60% phenolic: 40% squalene, where a clear decrease in the rate of disappearance of 9,10-dimethylanthracene can be seen. Aside from this result, the results of the other combinations show little to no change in the rate from the estimations.

However, it should be noted that the measured value at 40% phenolic: 60% squalene only just lies within the error of both the estimated and measured results. Thus it is possible that there may be some deviation with this mixture, although further data would need to be gathered to confirm this.

Even still, it appears that if there is a synergistic effect occurring between these two antioxidants it is likely occurring when the mixture contains around an even concentration of phenolic and squalene antioxidants.

Both the estimated and measured results follow the overall trend of decreasing rate of 9,10-dimethylanthracene disappearance as the proportion of squalene within the mixture increases. This is due to the significantly higher singlet oxygen quenching rate constant of squalene over the phenolic antioxidant, as seen from the individual quenching constant data from chapter 7.

8.1.6. Squalene and Sulfurized Olefin

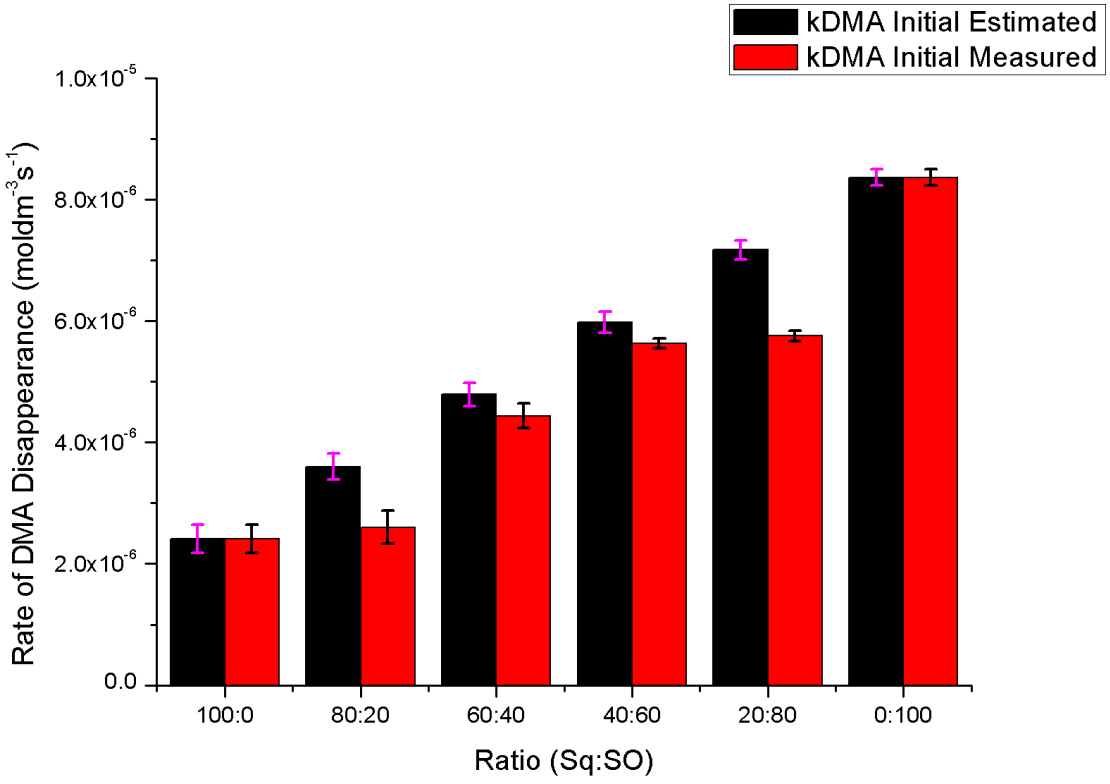


Figure 64 - Rate of DMA Disappearance vs Ratio Squalene to Sulfurized Olefin

It appears from the results obtained that there is a general decrease in the rate of 9,10-dimethlyanthracene disappearance for the antioxidant mixtures from the estimated values. This

is clearest at the 80:20 and 20:80 ratios respectively, where there is a significant decrease in the rate from the estimations.

The decrease in the rate at 40% squalene: 60% sulfurized olefin is not as distinct as those at the 80:20 ratios. However, the value does lie outside of the error for both the estimated and measured when looking directly at the data. The lower limit for the estimated value lies at around 5.81 $x10^{-6}$ $moldm^{-3}s^{-1}$ while the upper limit for the measured value lies at 5.71 $x10^{-6}$ $moldm^{-3}s^{-1}$, showing that there is indeed a significant enough decrease in the measured value.

The only mixture that does not show a certain decrease of the rate from the estimation is at 60% squalene: 40% sulfurized olefin where the observed change in within the error and therefore cannot be considered to be a significant deviation from the estimation. This combined with the smaller decrease noted at 40% squalene: 60% sulfurized olefin is interesting since it seems that whatever synergistic effect may be occurring here to reduce these rates has a greater effect when the concentration difference between the two antioxidants is greater.

The largest relative reduction from estimated values is at 80% squalene: 20% sulfurized olefin, which is approximately 27.8% lower than the estimated value while the relative reduction in the rate at 20% squalene: 80% sulfurized olefin is only approximately a 20% reduction.

8.2. Alternative Method

8.2.1. Aminic: Phenolic; Alternative Method

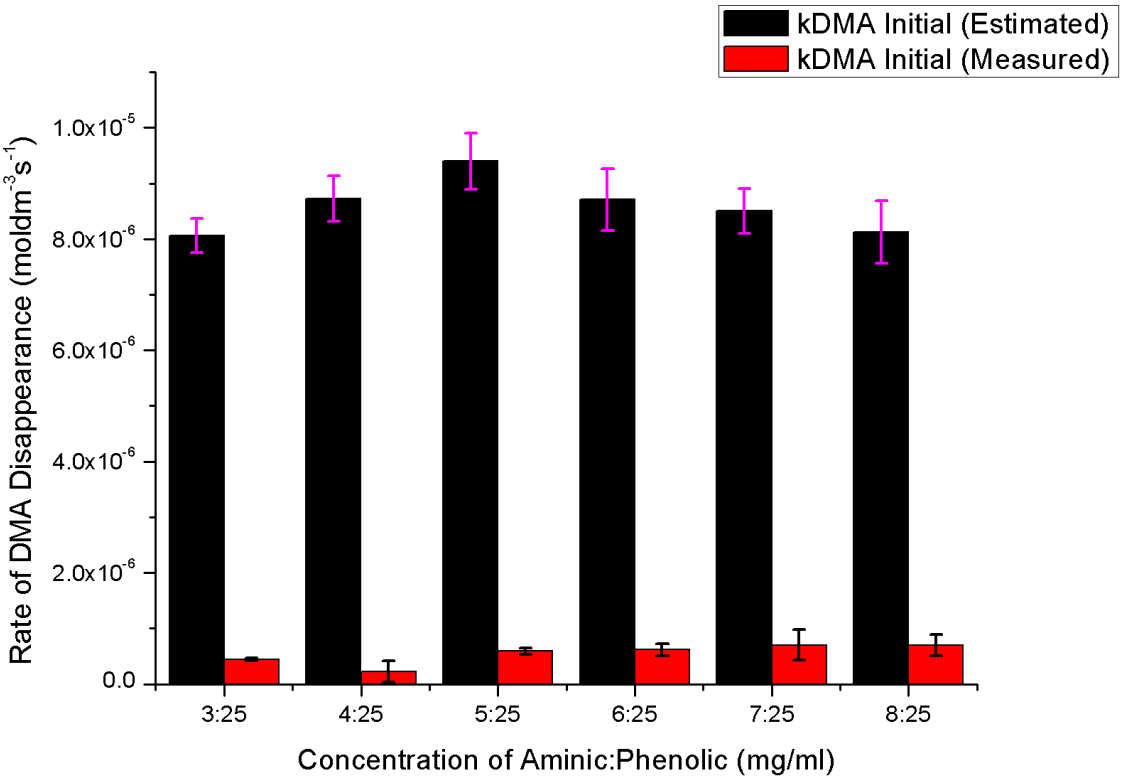


Figure 65 - Rate of DMA Disappearance vs Concentration of Aminic and Phenolic, Changing Aminic Concentration

From these results a very dramatic decrease in the rate of 9,10-dimethylanthracene disappearance from the estimated values can be seen. The decrease from the estimations is around an order of magnitude, suggesting a very significant synergistic effect occurring between the aminic and phenolic antioxidants.

The main issue that can be associated with the estimated values for the mixtures containing less than 5 mg/ml of the aminic antioxidant is that the estimated values for these had to be calculated from the individual quenching constant data for 5 mg/ml since the original data did not use these concentrations. This limits the accuracy of these values, but since the difference between the estimations and the measured values is so significant this does not impact the overall conclusions drawn from the data.

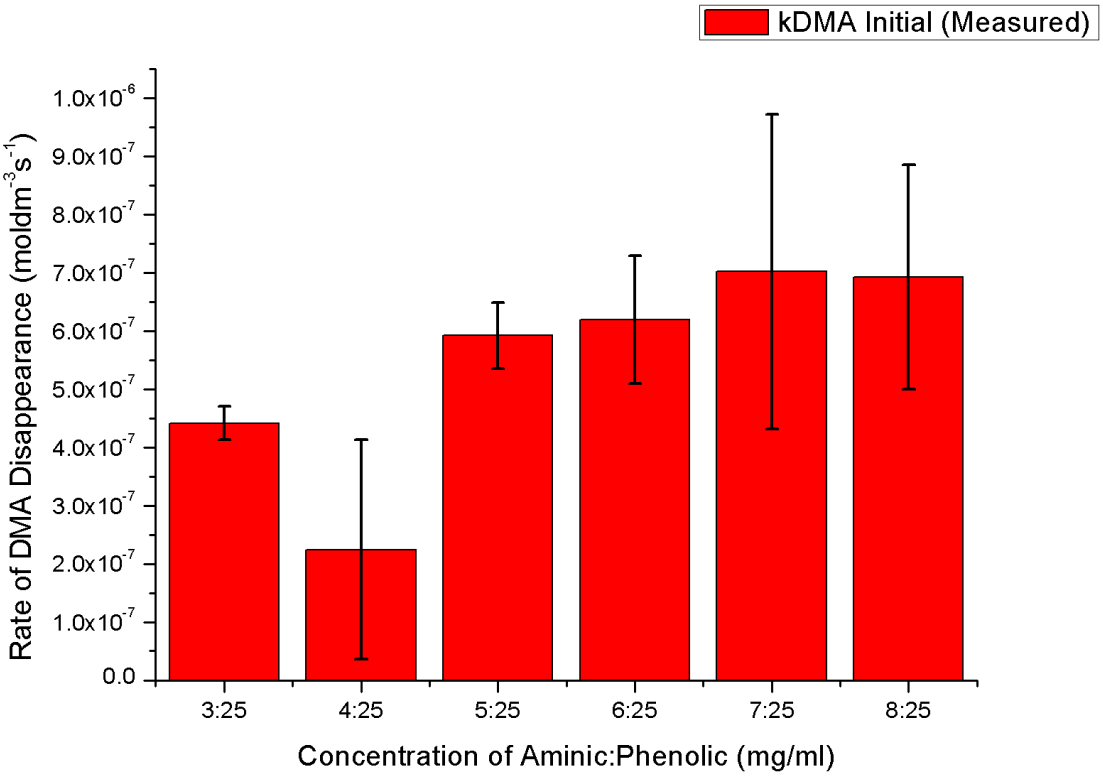


Figure 66 - Rate of DMA Disappearance vs Concentration of Aminic and Phenolic, Changing Aminic Concentration (Measured Values Only)

A closer look at the measured rates alone is shown in figure 66 where, aside from the values for 3:25 and 4:25, there appears to be no significant changes in the rates between the different mixtures. It is possible that the little visible change in the rate could be due to the small changes in the concentration in each mixture. Given that, unlike with the previous method, the overall concentration of the mixture is increasing as the aminic concentration is increasing it would be expected that the rate would decrease even if there is no synergistic effect, since there is a greater concentration of quenchers present.

An alternate explanation for the lack of significant change in the rate as the concentration increases could be that the quenching rate has reached a plateau, in that quenching is occurring almost as fast as singlet oxygen can be produced. To discern if either of these are the case further testing would be required. Ideally this would involve testing with lower overall concentrations of the mixtures to see if it is a case of quenching reaching a plateau, as well as allowing for a greater range of changes in the concentration of each mixture.

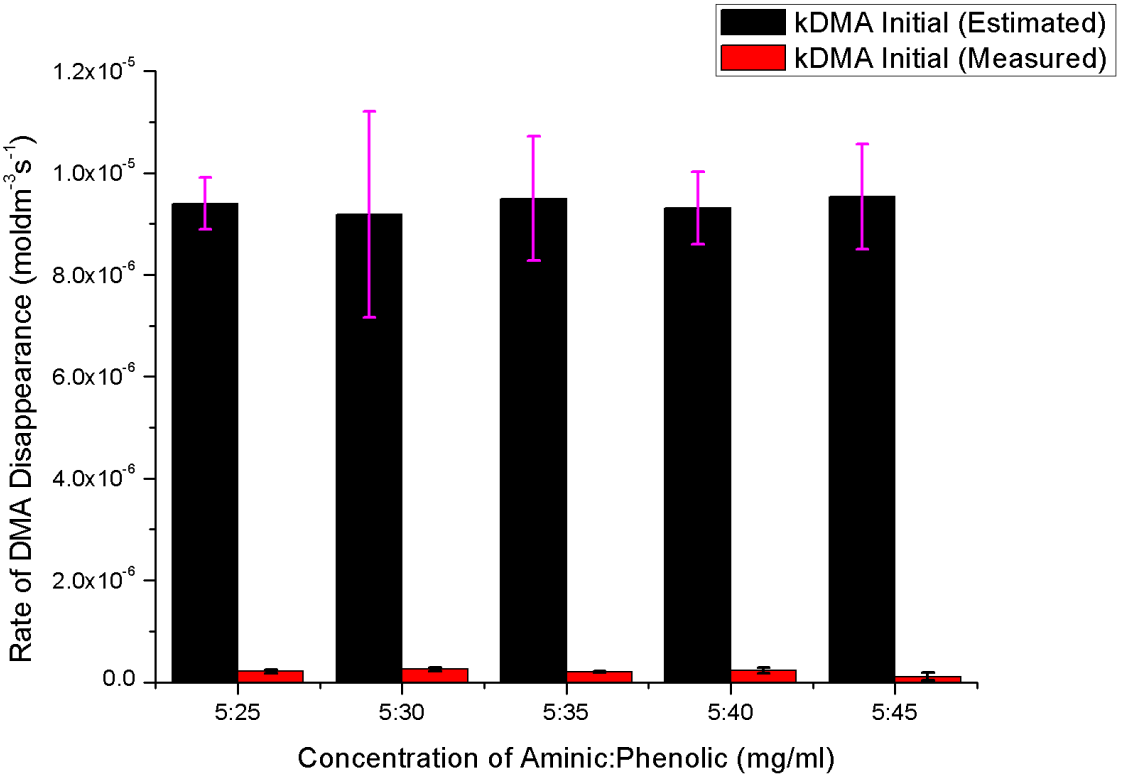


Figure 67 - Rate of DMA Disappearance vs Concentration of Aminic and Phenolic, Changing Phenolic Concentration

Again, as with the changing the aminic concentration, a very clear decrease in the 9,10-dimethylanthracene disappearance rate can be seen. The difference between the estimated and measured values when changing the concentration of the phenolic antioxidant is even greater than that seen when changing the aminic concentration.

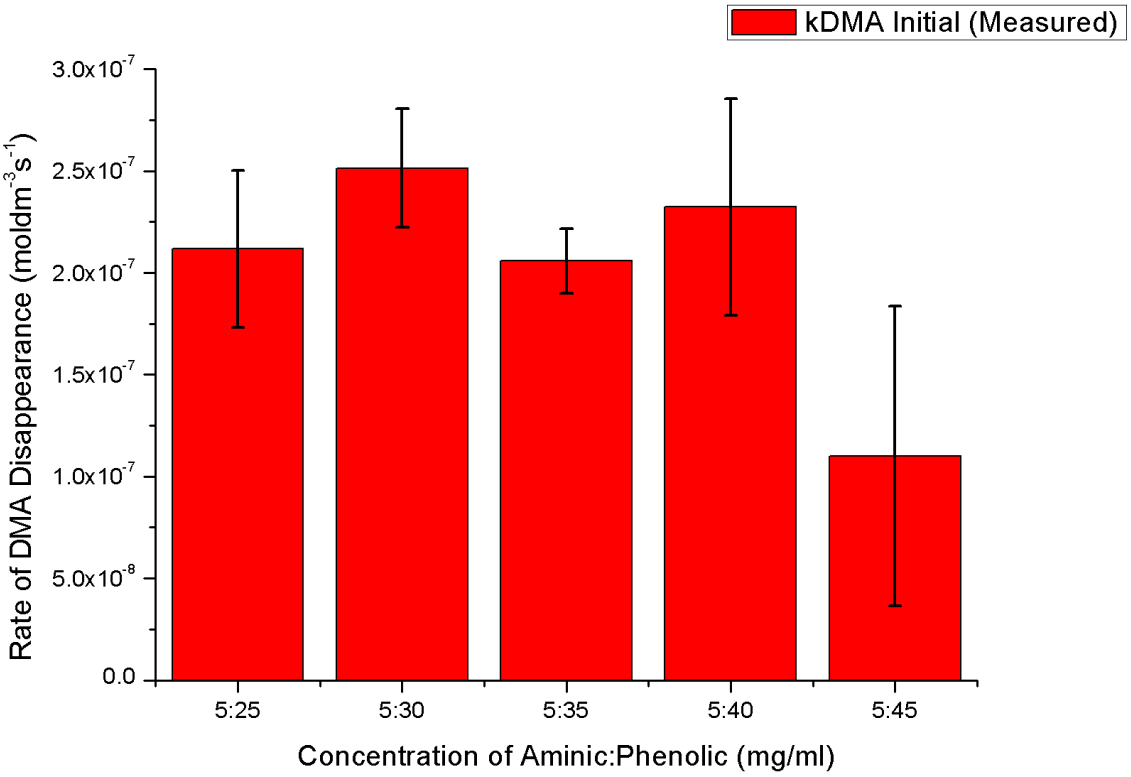


Figure 68 - Rate of DMA Disappearance vs Concentration of Aminic and Phenolic, Changing Phenolic Concentration (Measured Values Only)

Figure 68 shows just the measured data obtained when changing the phenolic concentration. Although at first glance it does appear that there is some fluctuation in the rates, most notably the drop in the rate at 5 mg/ml aminic: 45 mg/ml phenolic, almost all of the variations lie within the error at each concentration; the only exception being the aforementioned 5:45 concentration when compared to the rate at 5 mg/ml aminic: 30 mg/ml phenolic.

As stated earlier, not seeing a significant change in the rates between the concentrations is possibly due to a very high level of quenching occurring. Seeing the same effect occurring within both data sets therefore strongly supports this and the idea that it would be worthwhile to investigate the combination of these two antioxidants at lower concentrations to see how much of an effect changing the concentration may have on this synergistic effect.

8.2.2. Aminic: Squalene; Alternative Method

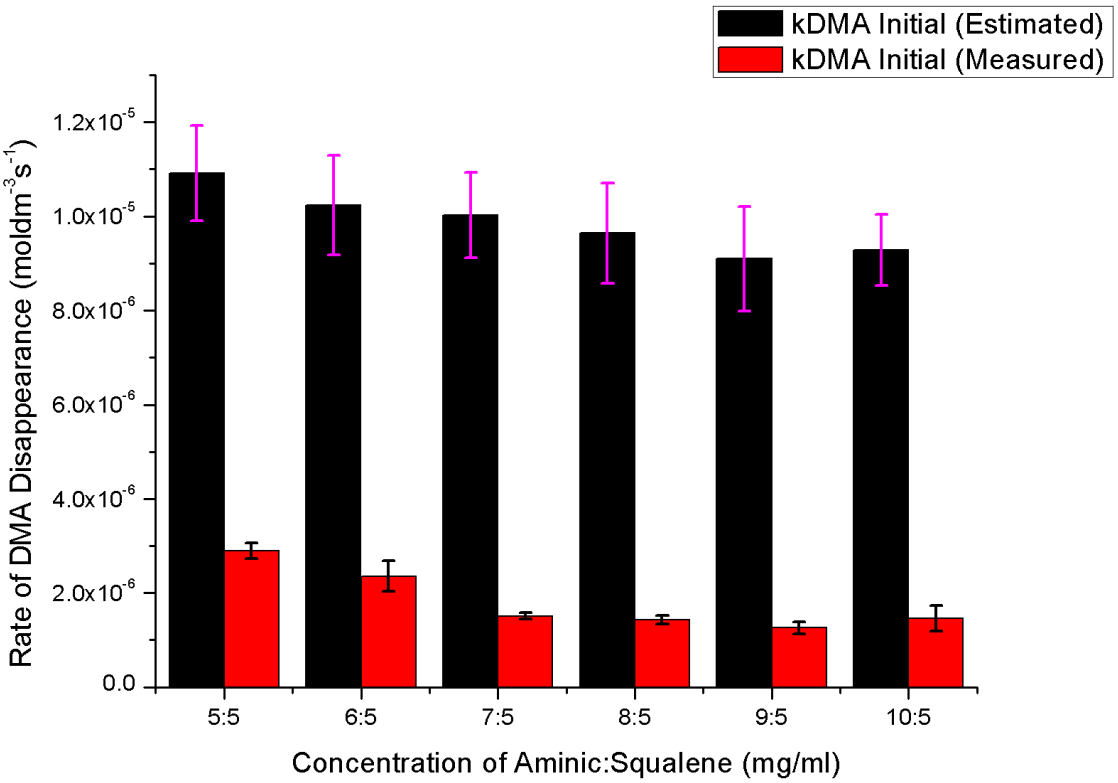


Figure 69 - Rate of DMA Disappearance vs Concentration of Aminic and Squalene, Changing Aminic Concentration

A clear decrease in the rate of disappearance of 9,10-dimethylanthracene can be seen for the aminic and squalene mixture across all of the various concentrations. This decrease is similar in nature to that seen with the aminic and phenolic mixture in that the rates seen are around an order of magnitude lower than the rates estimated for the mixtures.

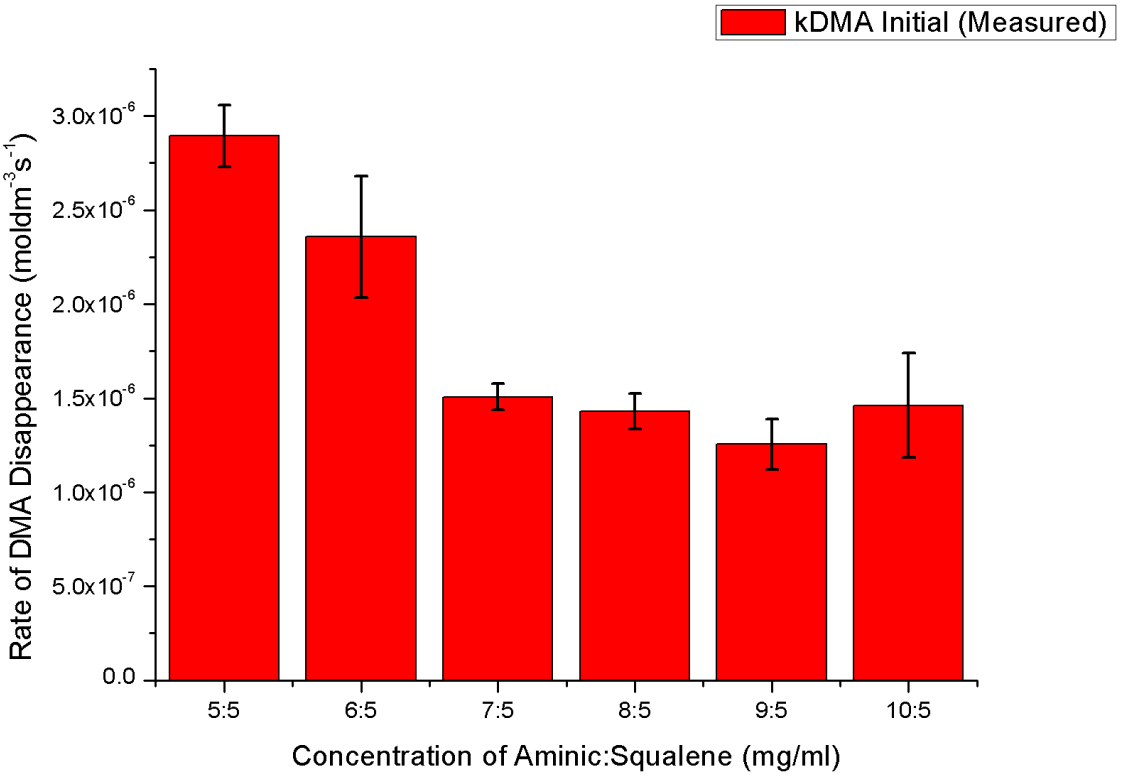


Figure 70 - Rate of DMA Disappearance vs Concentration of Aminic and Squalene, Changing Aminic Concentration (Measured Values Only)

Figure 70 gives a closer look at the measured values for this data set. The closer view allows for a clear view that after reaching 7 mg/ml aminic: 5 mg/ml squalene the rate plateaus with no significant change in the rate as the aminic concentration is increased further. There is however, a distinct decrease seen before this point between the mixtures containing 6 and 7 mg/ml. While there may also be a potential decrease in the rate when increasing the aminic concentration from 5 to 6 mg/ml the error associated with these measurements makes it unclear.

Comparing these results with the results from the aminic and phenolic mixture when changing the aminic concentration a clear trend is noticeable in that the rate appears to reach a plateau after a certain point. This again very much supports the theory that the quenching is occurring as fast as singlet oxygen is being produced.

It seems that the most effective use of this testing method would require running at lower concentrations when using the aminic antioxidant since it has such a strong quenching constant. It can also be noted that by decreasing the concentration to a range in which a change in the

quenching can be seen then it should theoretically be possible to obtain quenching constants for the mixtures.

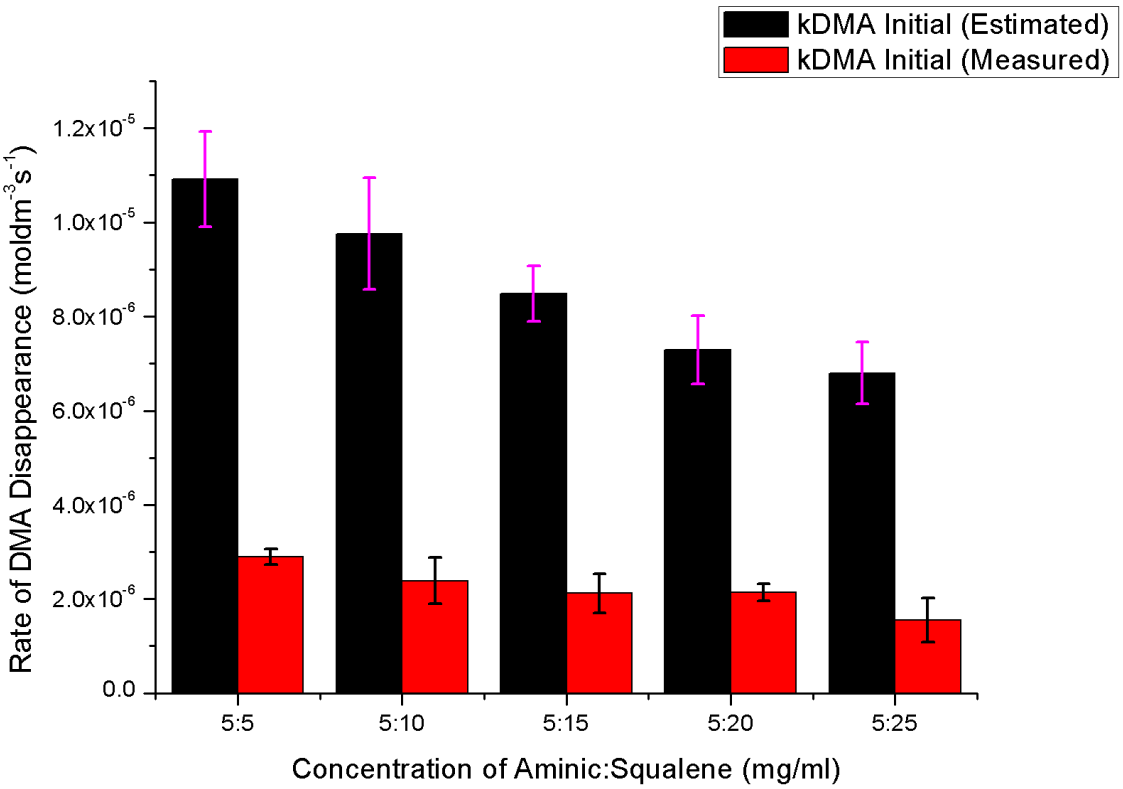


Figure 71 - Rate of DMA Disappearance vs Concentration of Aminic and Squalene, Changing Squalene Concentration

As with the results when changing the aminic concentration the rate of 9,10-dimethylanthracene disappearance is significantly lower than the estimations. Overall it does appear that there is less of a decrease in the rate with the increasing squalene concentration than was seen with increasing the aminic concentration. However, this is most probably due to the higher quenching constant associated with the aminic antioxidant rather than a synergistic effect.

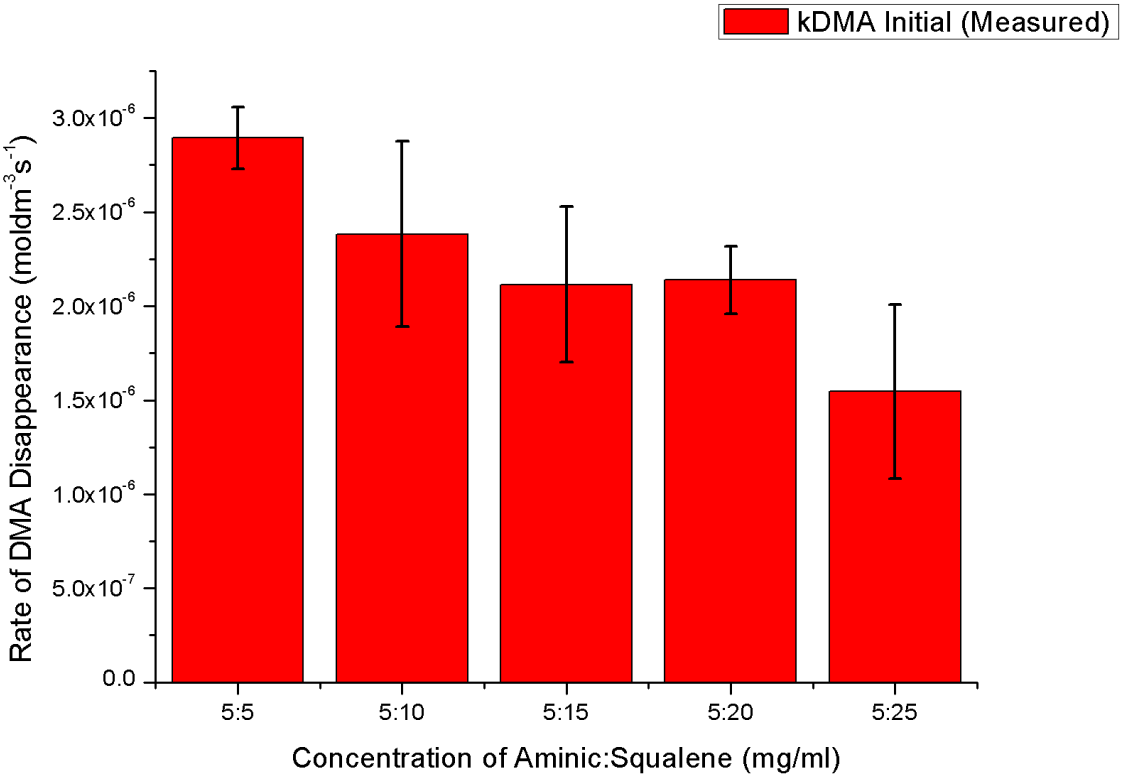


Figure 72 - Rate of DMA Disappearance vs Concentration of Aminic and Squalene, Changing Squalene Concentration (Measured Values Only)

Figure 72 shows the measured results when changing the squalene concentration in more detail. Due to the errors associated with the measured value the possible changes between many of the mixtures are not significant, with the first significant change only being apparent after an increase in the squalene concentration of 10 mg/ml. While it is possible that the rates may be plateauing, as seen with the other mixtures so far, it is also possible that the changes are not as apparent with the concentration increments used. Therefore, it may be beneficial, if these tests were to be repeated, to increase the increments for the change in the squalene concentration between mixtures, most likely from 5 mg/ml increments to 10 mg/ml.

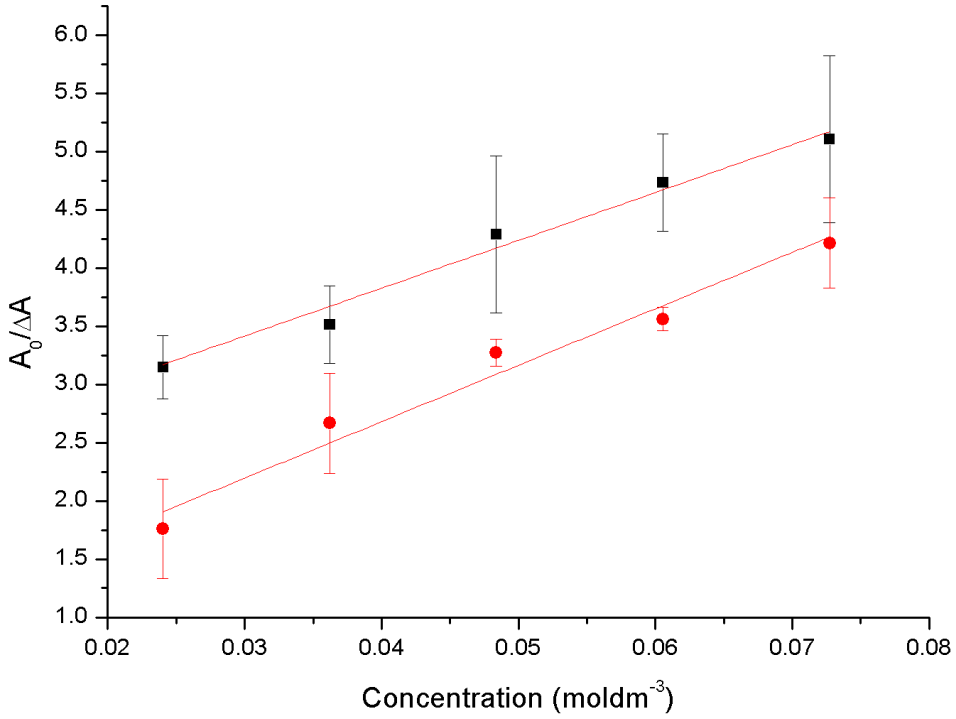


Figure 73 - $A_0/\Delta A$ vs Concentration of Aminic and Squalene, Changing Squalene Concentration

Table 44 - Quenching Constant Results for Estimated Values

Adjusted R-square	0.97331
	Value
Intercept	2.18445
Slope	41.07906
Calculated k_q	1.10×10^6 $mol^{-1}dm^3s^{-1}$

Table 45 - Quenching Constant Results for Measured Values

Adjusted R-square	0.97147
	Value
Intercept	0.74251
Slope	48.46785
Calculated k_q	3.83×10^6 $mol^{-1}dm^3s^{-1}$

The data gathered from changing the squalene concentration had sufficient data to allow for a precise calculation of the overall quenching rate constant for the mixture under these conditions using the method explained in chapter 7. Calculations were done for both the estimated and measured data for comparison, the results of which can be seen in table 45 and 46.

Interestingly, it appears that there is not a very large difference between the two values and it is possible that the change between them is within the margin for error. This would suggest that there is little to no synergistic effect occurring between the aminic antioxidant and squalene.

However, this does somewhat contradict the conclusions drawn from comparison of the initial rate constants, where a stark decrease in the rate of 9,10-dimethylanthracene disappearance was seen. This could possibly be put down to the fact that the estimations are based off of data that was gathered from a separate batch of work and therefore there could be some slight variations in the conditions, as well as the fact that there were less runs done for each of the combined antioxidant mixtures.

8.2.3. Phenolic: Squalene; Alternative Method

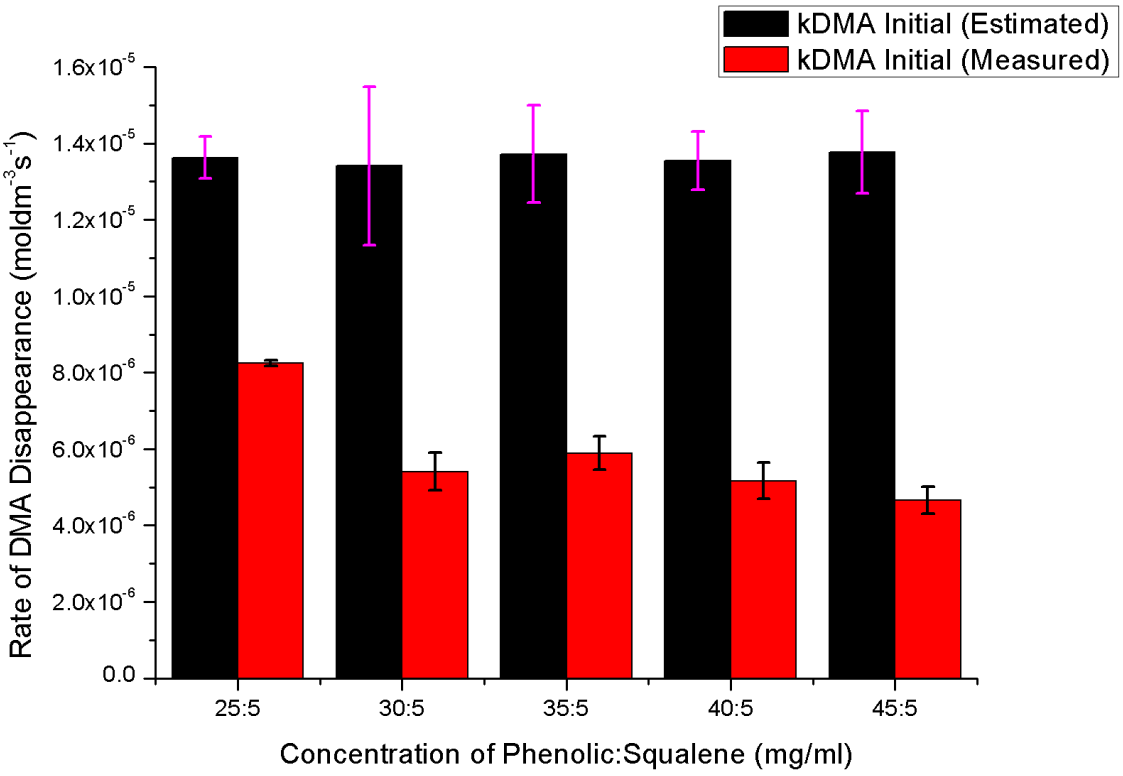


Figure 74 - Rate of DMA Disappearance vs Concentration of Phenolic and Squalene, Changing Phenolic Concentration

As has been seen with all of the other mixtures tested using this method there is a significant decrease in the 9,10-dimethylanthracene disappearance rate from those estimated. However, unlike with the other mixtures, the relative decreases do not appear to be as large, with the measured results only being approximately a half to a third of the estimations, while the aminic and phenolic combination yielded results around a tenth of the estimations.

This would suggest that the effect between the phenolic antioxidant and squalene is not as strong as with the aminic antioxidant present. This conclusion is also supported by the data from the first method, where very little deviation from the estimates was observed.

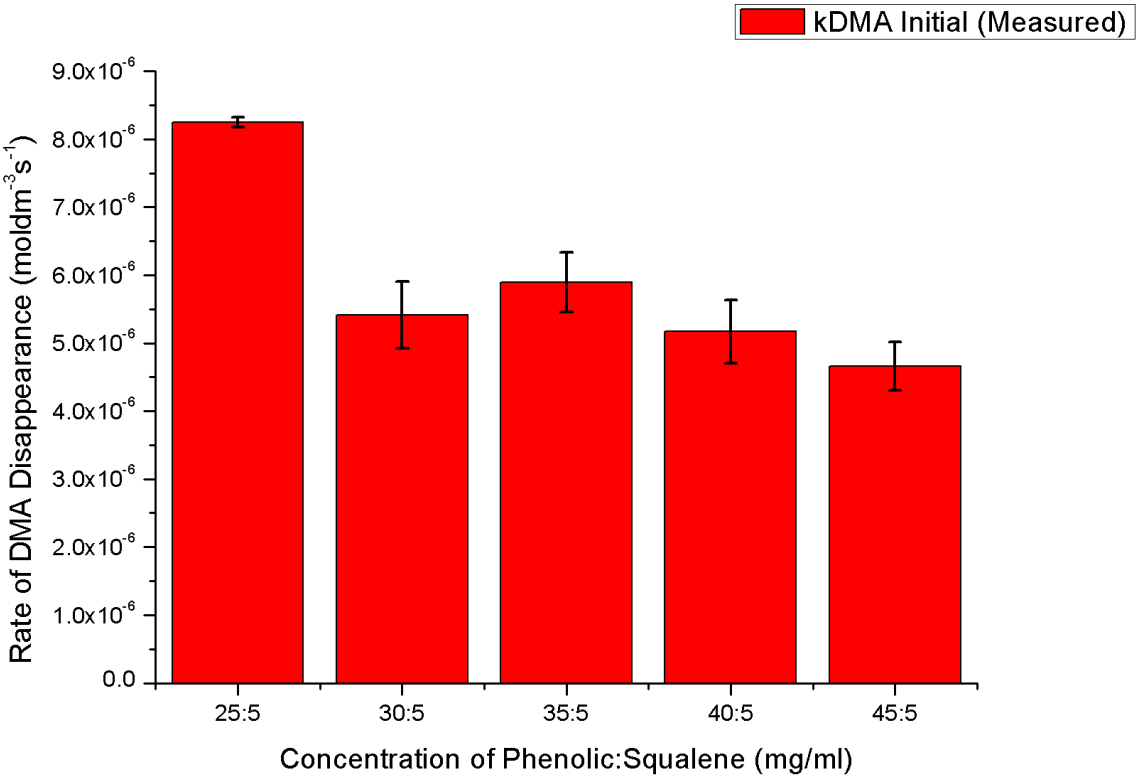


Figure 75 - Rate of DMA Disappearance vs Concentration of Phenolic and Squalene, Changing Phenolic Concentration (Measured Values Only)

A closer look at the measured values, figure 75, gives a clear view of there being very little deviation in the rate constant after the initial drop when increasing the phenolic concentration from 25 mg/ml to 30 mg/ml. Although another decrease can be seen between the rates at 35 mg/ml and 45 mg/ml. This could suggest that, similar to what was seen with the squalene data with the aminic and squalene mixture, the incremental increase in the concentration between

each mixture may be too small to see significant changes. Therefore, if these tests were to be rerun, it would be recommended to increase the increments from 5 mg/ml to 10 mg/ml.

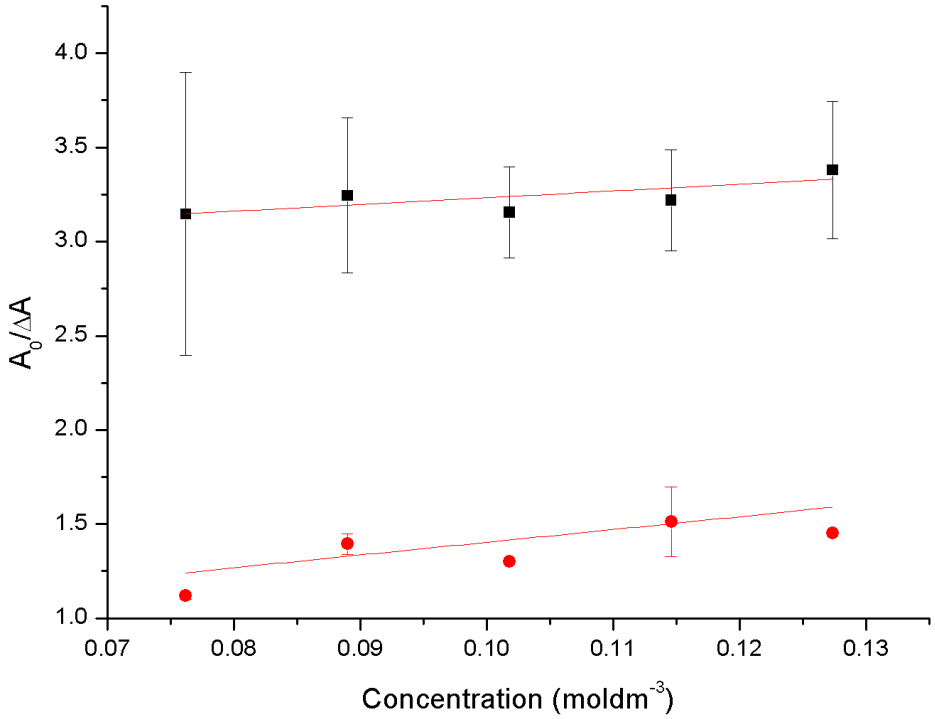


Figure 76 - $A_0/\Delta A$ vs Concentration of Phenolic and Squalene, Changing Phenolic Concentration

Table 46 - Quenching Constant Results for Estimated Values

Adjusted R-square	0.56105
	Value
Intercept	2.87489
Slope	3.58258
Calculated k_q	7.14×10^4 $mol^{-1}dm^3s^{-1}$

Table 47 - Quenching Constant Results for Measured Values

Adjusted R-square	0.62527
	Value
Intercept	0.72461
Slope	6.78635
Calculated k_q	$5.44x10^5$ $mol^{-1}dm^3s^{-1}$

The data gathered from changing the phenolic concentration with this mixture allowed us to follow through with the same analysis used for the measurements for the individual quenching constants, seen in chapter 7, a significant difference can be seen between the estimated k_q value and the one calculated from the measurements. The result for k_q calculated from the measured data is approximately an order of magnitude greater than that calculated from the estimations.

This is an interesting development since the first method of testing showed little signs of synergistic effect, the initial rate data suggested an improvement of two to three times what would be estimated. However, the significance of the difference between the quenching constants in greater than that. An explanation for this could be the fact that the initial rates only factor in the first section of the data set while the quenching constants were calculated from the whole data set, with small exceptions.

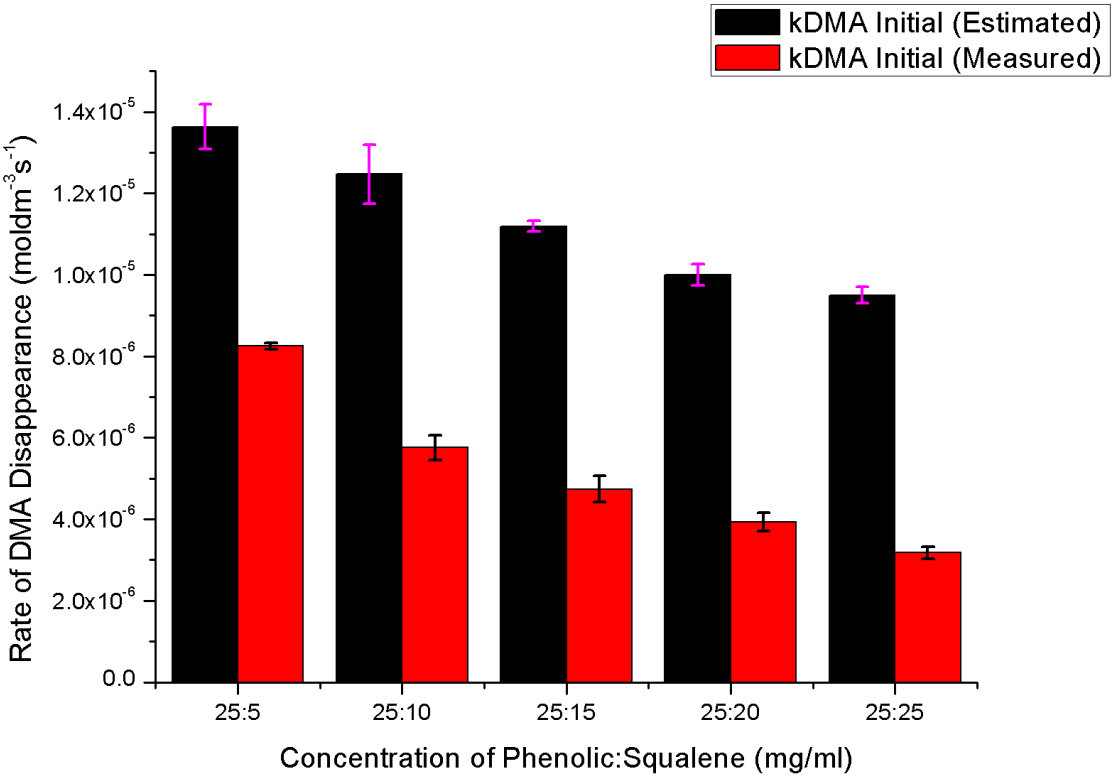


Figure 77 - Rate of DMA Disappearance vs Concentration of Phenolic and Squalene, Changing Squalene Concentration

When changing the concentration of squalene, a decrease in the initial rate of 9,10-dimethylanthracene disappearance can be seen across all of the mixtures. A gradual decrease in the rate can also be seen as the concentration of antioxidants increases, which is to be expected, although the rate seen at 25 mg/ml phenolic: 10 mg/ml squalene does deviate slightly with a lower rate than might be expected.

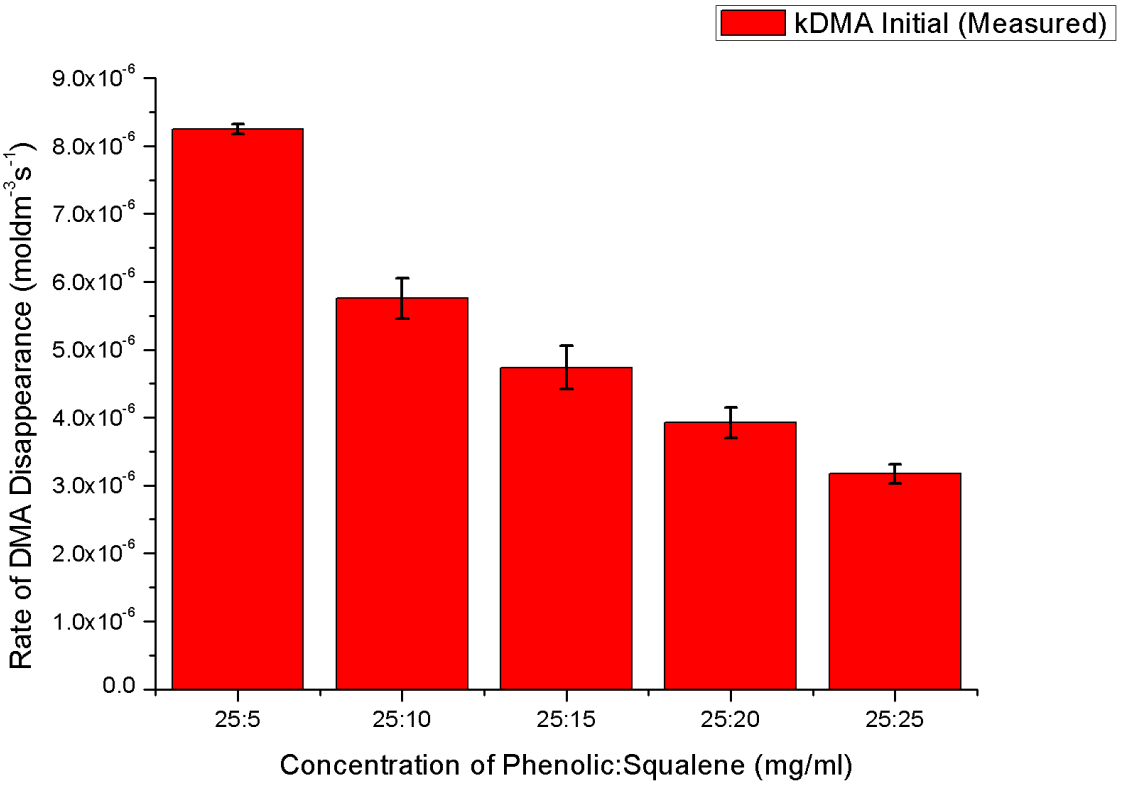


Figure 78 - Rate of DMA Disappearance vs Concentration of Phenolic and Squalene, Changing Squalene Concentration (Measured Values Only)

Looking closer at the measured data, figure 78, the downward trend in the rate constant can be seen more clearly. However, it does appear that there is curvature to this trend, with the most significant reduction in the rate occurring between the first two points. This could suggest that the rate is starting to reach a plateau point after the highest concentration measured here.

8.3. Conclusions

From the results seen from both methods there were signs of synergies occurring between a number of combinations of the antioxidants. This was especially so for the combination of the aminic and phenolic antioxidants, a conclusion which is understandable given that these two antioxidants are frequently utilised together within Lubrizol's additive formulations. As such it was confirmed by Lubrizol that they have seen signs of synergistic activity between these two antioxidants within their own in-house testing methods.

It was also suggested by Lubrizol that there might be synergies between the sulfurized olefin and the other two antioxidants since it is also frequently used in conjunction with the other antioxidants in additive formulations. However, it was not certain if this would be the case

since the sulfurized olefin is normally considered to be working as an antioxidant in a different way to the other two, as was discussed back in chapter 4, and as such it has not really been tested for synergistic effects in-house by Lubrizol.

Overall the two different methods have offered an interesting insight into potential effects of using multiple antioxidants in the same mixture on the overall singlet oxygen quenching efficiencies within said mixtures. However, there are still some limitations in that, while the data gathered can offer a starting point for further investigation, it is not possible to precisely identify what components of each mixture is responsible for any changes in singlet oxygen quenching efficiency.

To identify what is responsible for these effects other analytical techniques would have to be utilised to attempt to break down what is occurring within the mixture during the whole reaction process. Separation of the reaction mixture via chromatographic techniques could be useful in attempting to track any changes in the antioxidants themselves, or the formation of other products that could be having an effect on the quenching process.

Another significant difference with the data analysed is that while the estimates used for the first method where calculated from the data gathered within each set, and thus was gathered within the same time period as the rest of the data, the estimates for the second method were calculated from the data used to determine the individual quenching constants, which had been gathered prior to these experiments.

While this difference should not have too much of an effect on the overall outcomes of the analysis, it should be noted that there is a small possibility of differences to the outside conditions of the runs which may cause some variation.

The most significant point of note from all of the data gathered from the second method is that the singlet oxygen quenching efficiencies of the antioxidants being used need to be taken into account more. Since the aminic antioxidant is a significant quencher, when it was combined with the phenolic antioxidant and a synergistic effect was added to this as well, it became impossible to see significant variation as the concentrations were altered.

However, when the phenolic antioxidant and squalene, which both showed lower singlet oxygen quenching in individual testing, were combined there was still enough interaction

between the 9,10-dimethylanthracene and singlet oxygen occurring that changes in the singlet oxygen quenching could be observed as the concentration was altered.

An interesting idea into further exploration of potential synergies between these antioxidants would involve a combination of the two methods tested during this research. By selecting a ratio of the antioxidants which showed signs of a synergistic effect and changing the overall concentration of the mixture, whilst maintaining the individual ratios, it could be possible to calculated quenching rate constants for combinations of interest at the ratios which showed the greatest signs of synergy.

9. Results and Discussion IV: Attempting to Develop a Method to Separate Physical and Chemical Quenching Constants

It was of significant interest to this project to attempt to separate out the physical and chemical components of the overall quenching constant for each of the antioxidants tested. This however, proved difficult due to the impurity of the Lubrizol samples provided, as discussed in chapter 7 when calculating the individual quenching constants. The impurities within these samples made it difficult to determine an exact wavelength at which to measure their absorption as well as fluctuations within the runs themselves, as will be shown later in this chapter.

However, a method by which to compare the effect of chemical quenching against physical quenching was suggested, even if not fully applicable for the data gathered thus far. As such this could be utilised at a later point with further data gathering. It is known that 9,10-dimethylanthracene readily reacts with singlet oxygen and so it can be assumed that it is primarily a chemical quencher of singlet oxygen. Therefore by calculating the rate of reaction of 9,10-dimethylanthracene with singlet oxygen and comparing this to the overall singlet oxygen quenching taken from literature[32] the proportion of singlet oxygen quenching that can be attributed to chemical quenching can be obtained.

For the time being, to give a rough idea of the level of chemical quenching that may be occurring with the antioxidants tested in this study, plots of the normalised absorbance vs. irradiation time were made. Any significant changes in the absorbance over time would suggest with a high level of certainty that chemical quenching is occurring to a significant degree. Enough so to warrant closer investigation as to how strongly the chemical quenching effects the overall singlet oxygen quenching efficiency of the antioxidant.

Initially, testing was required to find a suitable concentration of the antioxidant to register the absorbance at a level that changes could accurately be detected. However, this posed a challenge with the Lubrizol antioxidants as, in all three cases, the concentration had to be dropped to a level a lot lower than was used to calculate the individual quenching constants. The concentrations used will be discussed further alongside the discussion of the antioxidants results later in this chapter.

While chemical quenching can be a very effective method of singlet oxygen quenching, in the case of working within an engine oil chemical quenching would not be the preferred method of singlet oxygen quenching. This is due to the limited nature of what can be added to the lubricant formulation and the difficulties in ensuring that a large enough concentration of a chemical quencher would still be present within the lubricant after a period of use. It would also be very important to be aware of any potential by-products that may form from chemical quenching since these by-products could potentially go on to react further with other compounds that may be found within the lubricant, potentially causing other problems.

On the other hand, physical quenchers would not be potentially nullified after the initial quenching, it would be expected instead that after a period of time the energy absorbed by the quencher would be dissipated into the solvent, in this case the base stock, and the quencher could function again.

9.1. Aminic

Initial tests to find a suitable wavelength to measure at, as well as a suitable concentration of the aminic antioxidant for test were conducted. Given the dark colouration of the aminic antioxidant it was clear that the concentration that could be used for testing would not be able to be very high. This proved correct and a concentration of 0.01 mg/ml was used for testing. It should also be noted that the wavelength used for measurements was 290nm.

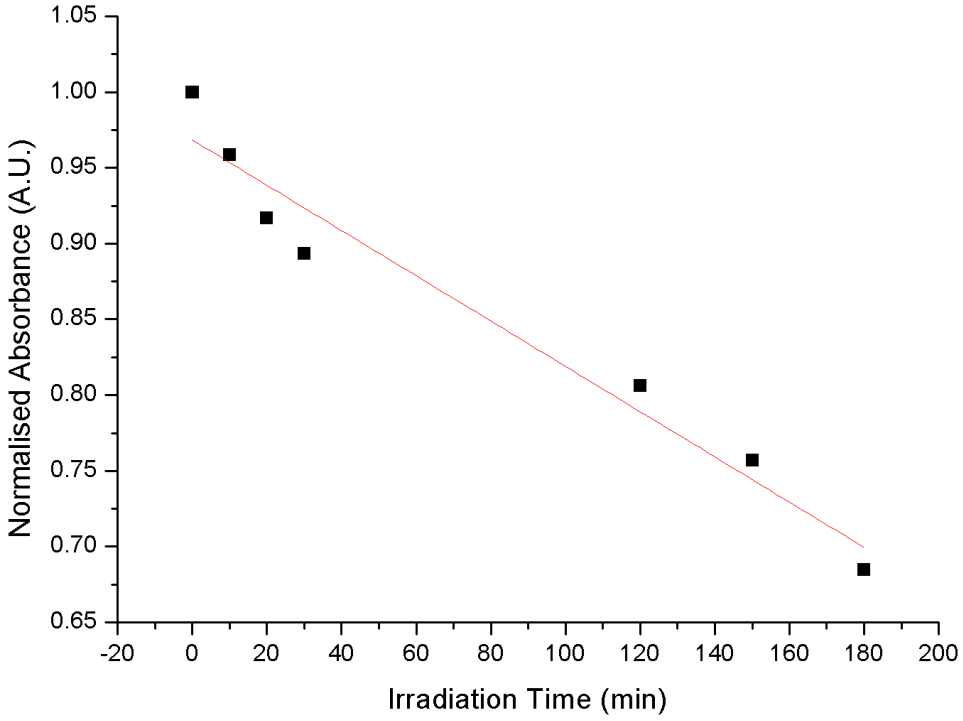


Figure 79 - Normalised Absorbance vs Time for Aminic Sample (Run 1)

Table 48 - Results of Normalised Absorbance vs Time for Aminic (Run 1)

Adjusted R-square	0.95274
	Value
Intercept	0.96839
Slope	-0.00149 s^{-1}

From the plot for the first set of data gathered there was an obvious negative trend to the data over the period of 180 minutes. Overall the absorbance at 180 minutes was 32 percent lower than the initial absorbance suggesting that there was at least some chemical reaction occurring.

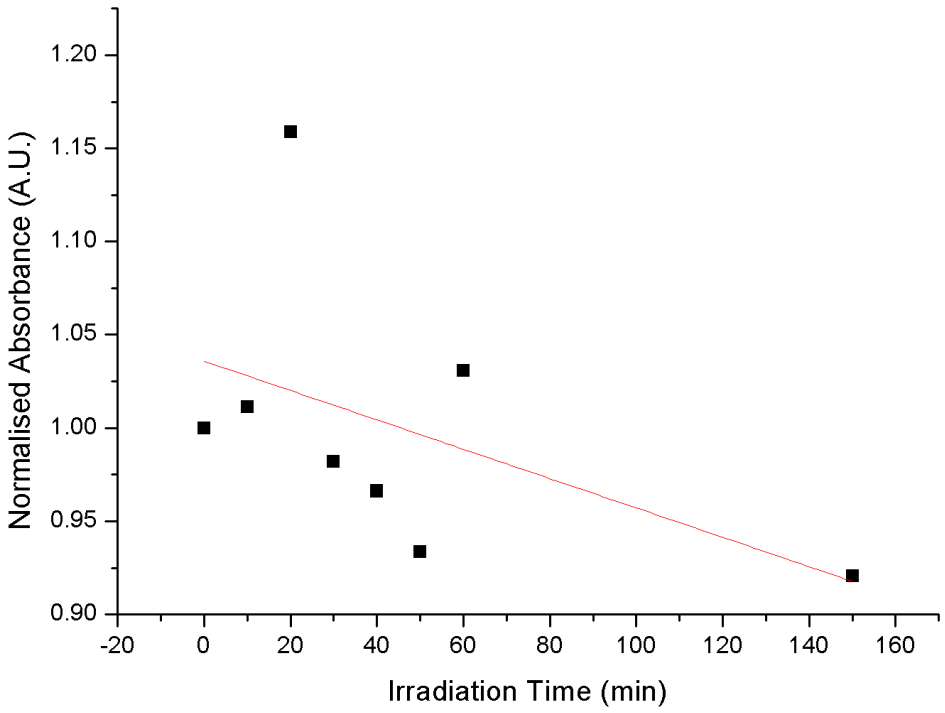


Figure 80 - Normalised Absorbance vs Time for Aminic Sample (Run 2)

Table 49 - Results of Normalised Abosrbance vs Time for Aminic Sample (Run 2)

Adjusted R-square	0.12287
	Value
Intercept	1.03588
Slope	-7.87257 x 10^{-4} s^{-1}

In contrast to the first test with the aminic antioxidant the second test showed a lot more fluctuation in the absorbance. However, a general slight negative trend can still be seen even with the noise. The difference between the plots of these two runs could be attributed to the impurity of the Lubrizol antioxidants. While the aminic antioxidant was not suggested have the most impurities, it was stated that there was a likelihood of some impurities in the form of unreacted or not fully reacted material, as discussed in chapter 4. These impurities are a problem that will need to be overcome if accurate measurements are to be attainable.

Another factor that might need to be addressed is the fact that such small concentrations of the aminic antioxidant are needed to be able to register low enough for accurate measurements to

be taken. With such small concentrations, it is hard to see any real change in the concentration since even large changes in the absorbance may not be as significant as they appear given the very low concentration.

Unreacted diphenylamine	0.7%
Monoalkylated on phenyl	21.9%
Monoalkylated on nitrogen (assumed)	2.4%
Dialkylated on phenyl	64%
Dialkylated with one alkyl on nitrogen (assumed)	7.4%
Trialkylated total	3.5%

9.2. Phenolic

After initial testing the concentration decided upon for testing was 5 mg/ml and the wavelength to measure at was taken as 316nm. Again, as with the aminic antioxidant, the concentration used for these tests had to be lowered in order to be able to accurately measure the absorbance.

The phenolic antioxidant yielded some very interesting results in both data sets that were gathered. As can be seen in figure 81 initially there is a clear and linear decrease in the normalised absorbance until 60 minutes of irradiation. However, after this point the opposite is true and a very clear, linear positive trend is seen up until 255 minutes of irradiation.

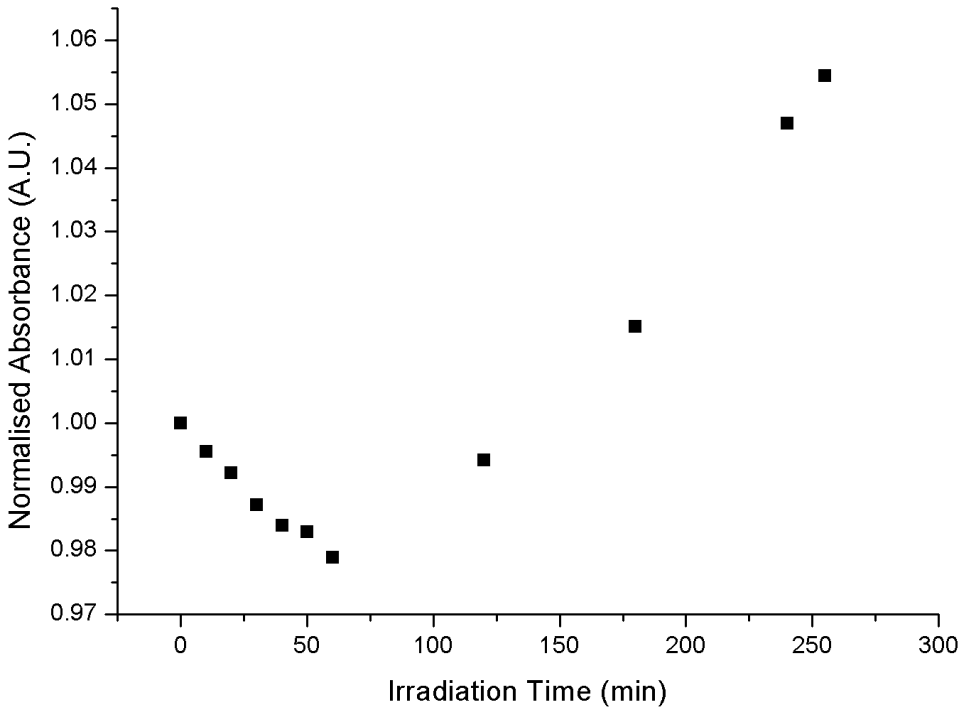


Figure 81 - Normalised Absorbance vs Time for Phenolic Sample

The linear trend seen in the first 60 minutes is shown more clearly in figure 82 with an R-square value of 0.97707. However, while there is an obvious decrease in the absorbance, the overall change in the absorbance between the initial and the value at 60 minutes in only a change of 2.2%. This could suggest that while there may be some chemical quenching occurring it is not likely to be a large proportion of the overall quenching seen for the phenolic antioxidant.

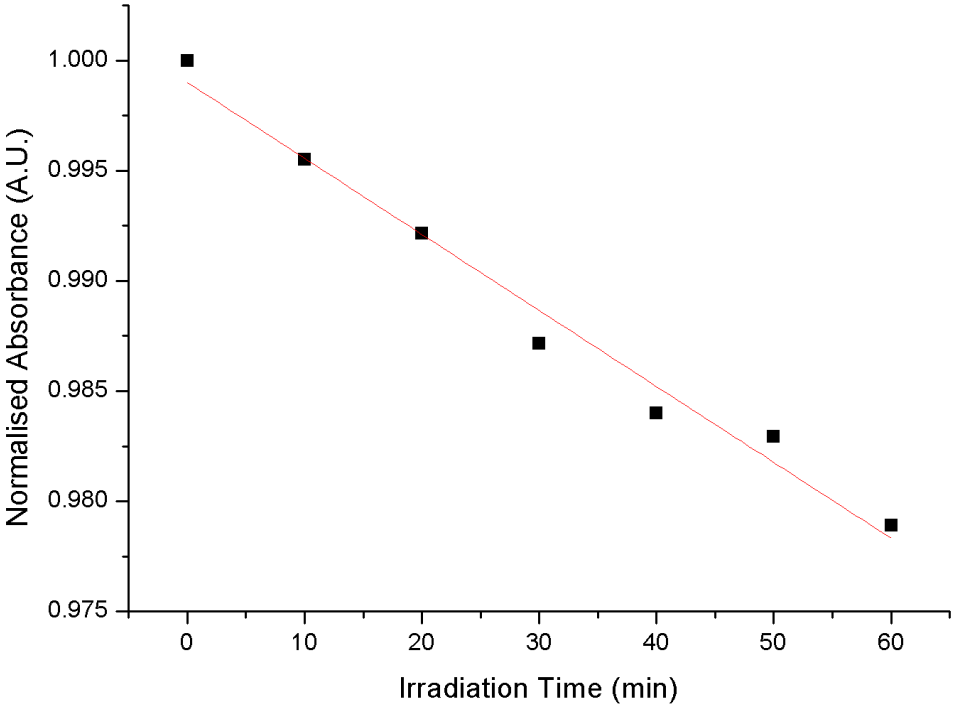


Figure 82 - Normalised Absorbance vs Time for Phenolic Sample (First 60 mins)

Table 50 - Results for Normalised Absorbance vs Time for Phenolic Sample (First 60 Mins)

Adjusted R-square	0.97707
	Value
Intercept	0.999
Slope	-3.4475 x 10^{-4} s^{-1}

In the second portion of the data there was a very clear and strong increase in absorbance at 316nm. Given how long it took for an increase in the absorbance to be seen, along with the initial decrease seen in the absorbance, might suggest that a reaction is indeed taking place but that it is a secondary reaction that is being seen here.

The reasoning for this is that the nature of the initial decrease and the fact that it is linear with a negative slope is most likely due to an intermediate state being formed upon reaction with singlet oxygen. If this intermediate then goes on to react further, it would appear that the product of this secondary reaction absorbs strongly in the same region as the phenolic antioxidant; hence the increase in the absorbance seen in the full plot.

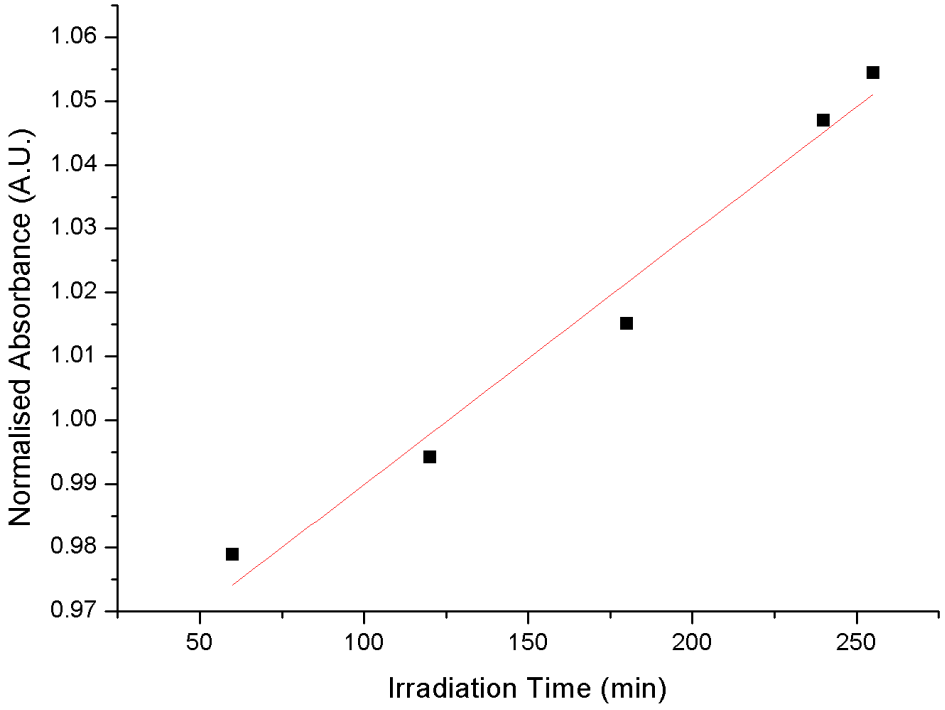


Figure 83 - Normalised Absorbance vs Time for Phenolic Sample (60 - 255 mins)

Table 51 - Results from Normalised Absorbance vs Time for Phenolic Sample (60 - 255 mins)

Adjusted R-square	0.97179
	Value
Intercept	0.95046
Slope	3.94673 x 10^{-4} s^{-1}

If this increase in absorbance is indeed due to product formation then another testing method may be required to fully understand the extent of the chemical quenching occurring, since the product formation is clearly interfering with the measurement of the phenolic antioxidant's absorbance.

In this case, it might be most beneficial to explore the options available possibly utilising chromatography to try and determine the extent of the chemical reaction occurring.

9.3. Sulfurized Olefin

Initial testing determined that a suitable wavelength to measure at was 290nm and an appropriate concentration to use was 0.5 mg/ml. At this concentration, the initial absorbance was close to 1, however, this concentration is significantly lower than the concentrations used for calculating the individual quenching constants.

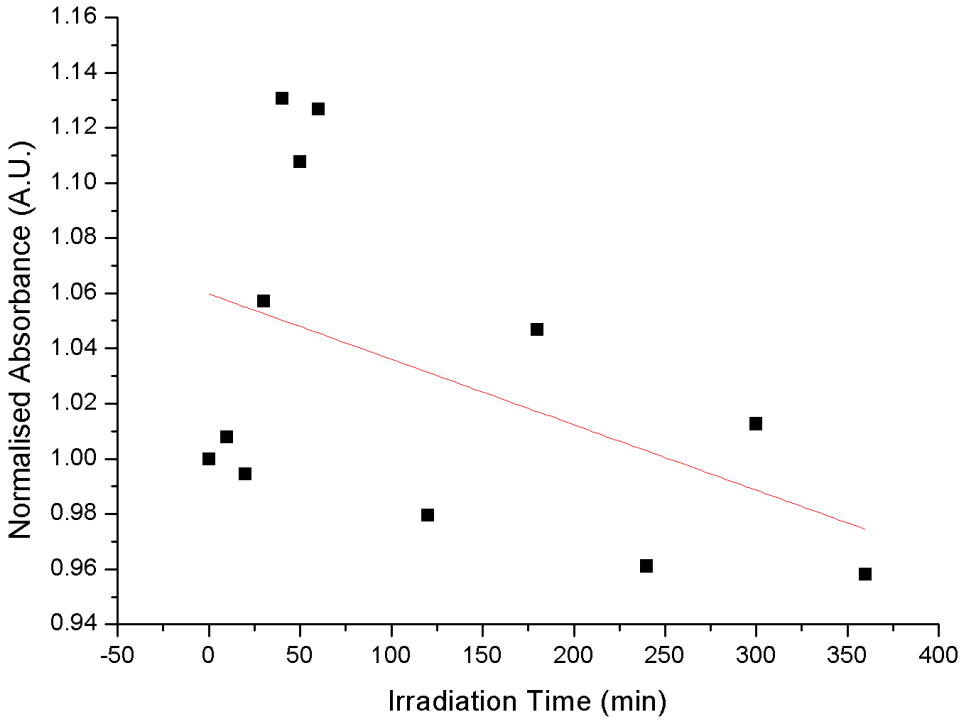


Figure 84 - Normalised Absorbance vs Time for Sulfurized Olefin Sample (Run 1)

Table 52 - Results from Normalised Absorbance vs Time for Sulfurized Olefin Sample (Run 1)

Adjusted R-square	0.14719
	Value
Intercept	1.0598
Slope	-2.37201×10^{-4} s^{-1}

In both runs there was a fair amount of fluctuation of the absorbance over time. Despite this there does appear to be a slight negative trend in the absorbance as the irradiation time increases. However, this decrease in the absorbance over time is very minor with the absorbance only

decreasing by 5% over 360 minutes in the first run, and slightly more so at 14% in the second run.

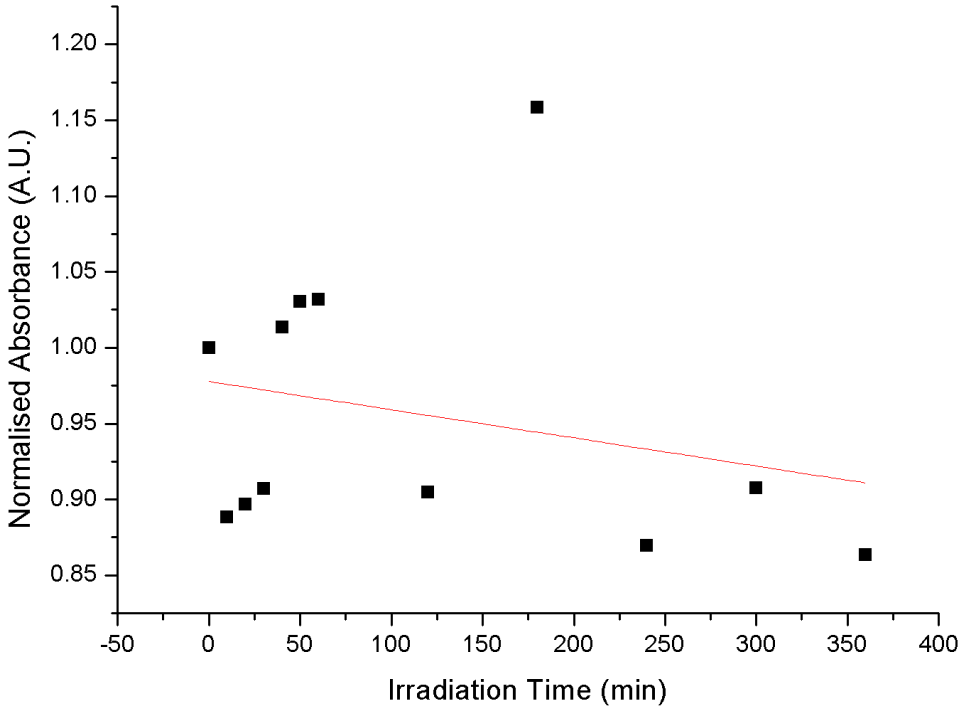


Figure 85 - Normalised Absorbance vs Time for Sulfurized Olefin Sample (Run 2)

The fact that there is so much fluctuation within the absorbance, along with little overall change in the absorbance, could be the result of product formation occurring and absorbing around the same wavelength as the sulfurized olefin; as was suggested earlier with the phenolic antioxidant.

Since there is not as clear a decrease followed by an increase it is unlikely that any product is absorbing more strongly than the sulfurized olefin at this wavelength. Although it could be possible that there is still an intermediate state being formed, that may be responsible for the increases seen, while the final product of the reaction may not absorb at the same wavelength, or may not absorb as strongly, hence the overall trend is still towards the negative.

Closer inspection of the UV-Vis spectra might give some indication if this is the case. However, with the fact that the sulfurized olefin is known to have a higher chance of impurities in samples, the UV-Vis spectra may be too difficult to determine any new peaks. As such chromatographic

methods, may be a better indication of product formation occurring, which will be discussed in chapter 10.

9.4. Squalene

The wavelength selected for measurements after initial testing for squalene was 289 nm using a concentration of 30 mg/ml since this concentration gave an initial absorbance around 0.5. Unlike with the Lubrizol antioxidants the concentration used for testing here was actually higher than the concentrations used to calculate the individual quenching constant.

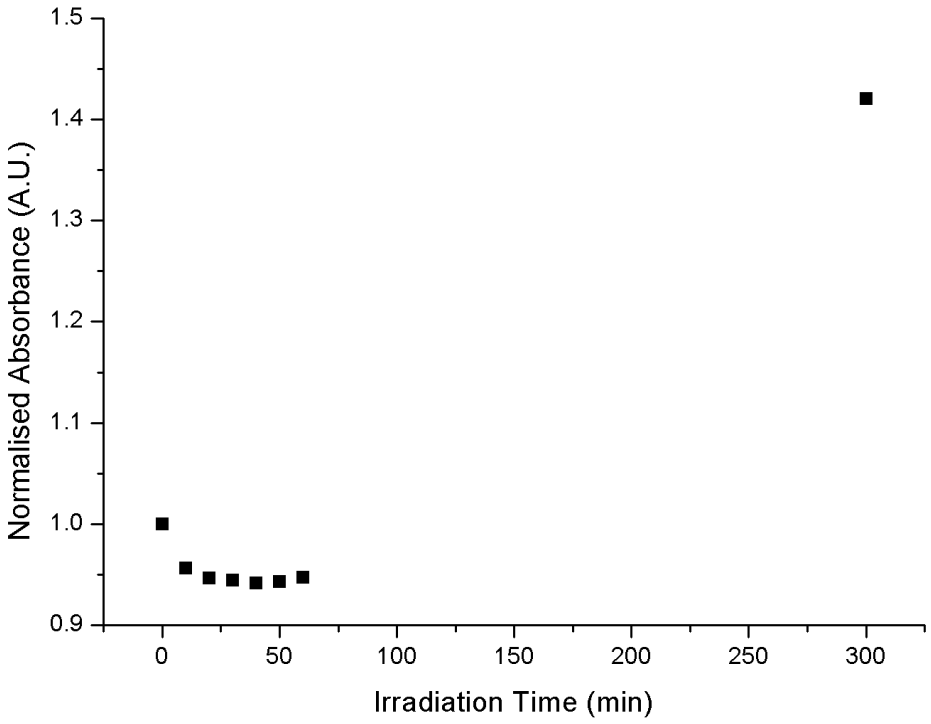


Figure 86 - Normalised Absorbance vs Time for Squalene (Run 1)

In the first run, there is a very clear and drastic increase in the absorbance of 42% after irradiating the sample for 360 minutes. However, it is not possible to determine if this is a trend similar to that seen with the phenolic antioxidant or just an anomalous result due to no measurements being taken between 60 and 360 minutes.

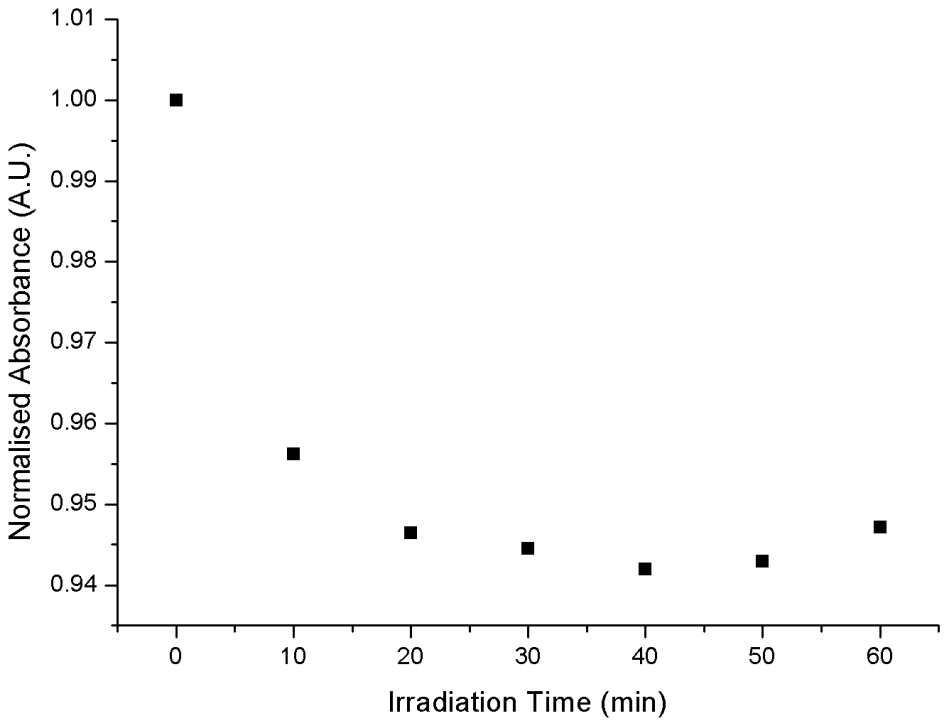


Figure 87 - Normalised Absorbance vs Time for Squalene (Run 1, First 60 mins)

A closer look at the initial irradiation period of the first run shows an initial decrease that lessens as the irradiation period goes on, as well as some signs of an increase in the absorbance towards 60 minutes. Over the 60-minute period however, the absorbance only decreases by 6%, which does not seem to be a very significant change.

This coupled with the lessening of the decrease in the absorbance after 20 minutes may suggest that little to no chemical quenching is occurring with squalene. Alternatively, it may suggest that if chemical quenching is occurring then the product being formed is absorbing at the same wavelength as squalene which is why there is no apparent change in the absorbance.

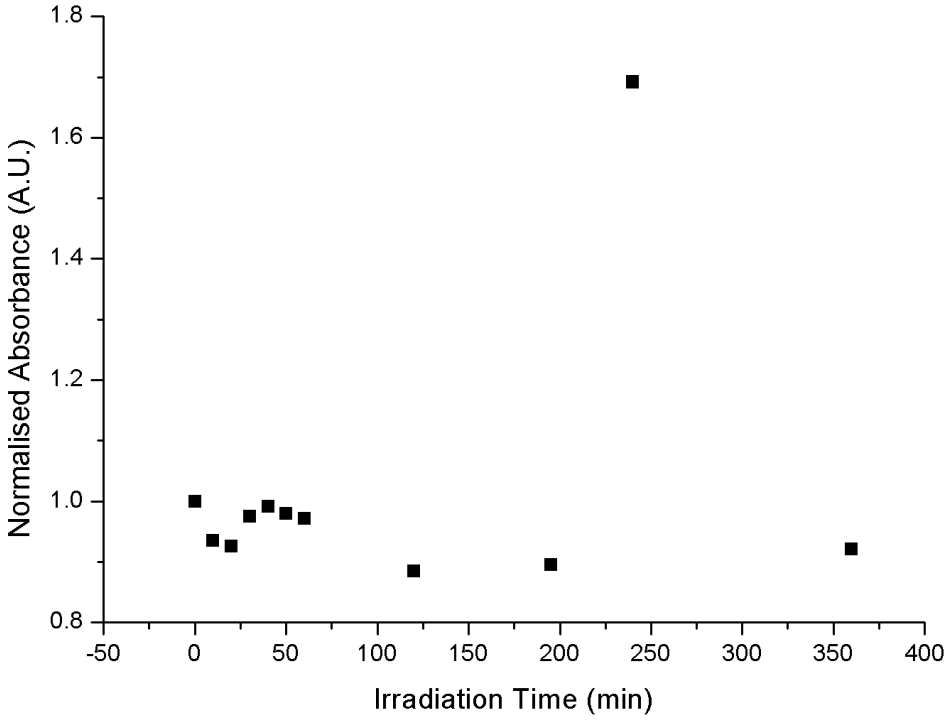


Figure 88 - Normalised Absorbance vs Time for Squalene (Run 2)

Unlike with the first run testing squalene there was no increase of the absorbance at 360 minutes. There was however, an anomalous result at 240 minutes which was ignored in further analysis of the run, as seen in figure 89.

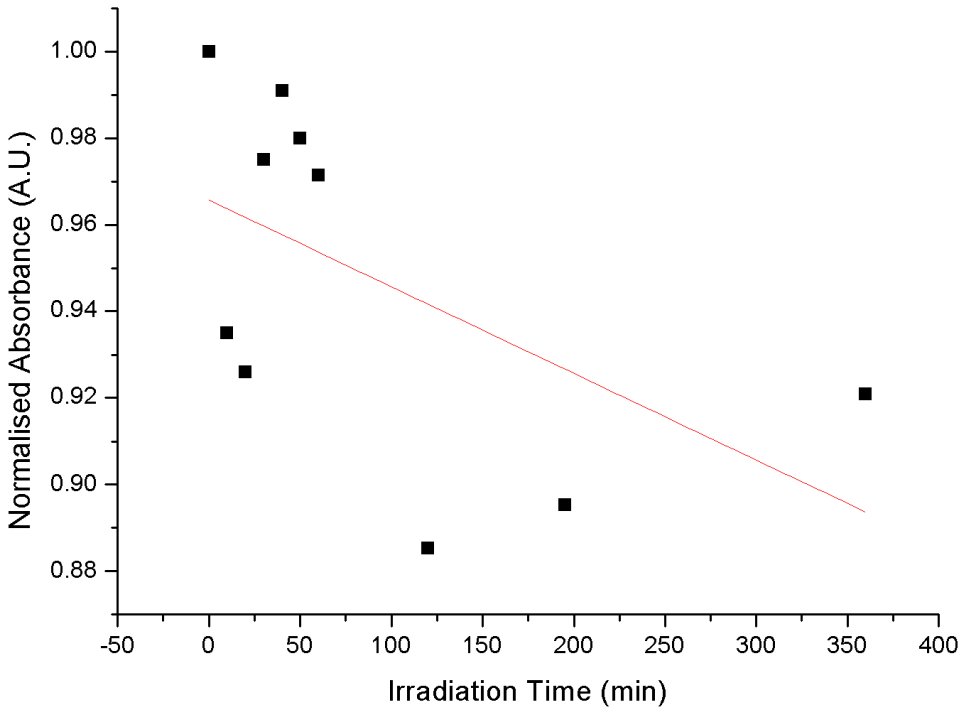


Figure 89 - Normalised Absorbance vs Time for Squalene (Run 2, Result Omitted)

With the anomalous result removed it is possible to get a better look at the changes in the absorbance over the irradiation period. There was a lot more variation in the results for the second run, with no obvious trend in the first 60 minutes, unlike in the first run. Instead there is more noticeable fluctuation in the absorbance, especially across the first 30 minutes.

This makes it less likely that a product is forming that is absorbing at the same wavelength as squalene since the decrease is initially noticeable, as well as the decrease at the later irradiation times. The overall decrease in the absorbance for this run was only 8%, however, the lowest absorbance seen was after 120 minutes of irradiation and was 12% lower than the initial absorbance.

Overall, it certainly appears that there may be some chemical reaction occurring over prolonged irradiation. However, closer investigation of the spectra as well investigation through chromatography, which will be discussed in chapter 10, may help to determine if the changes in absorbance are only due to the disappearance of squalene or if product formation is affecting the results.

9.5. α-Tocopherol

After initial testing the wavelength chosen for measurements of α-tocopherol was 294nm and α-tocopherol was tested at a concentration of 0.05 mg/ml. This was comparable to the concentrations used for calculating the individual quenching constant.

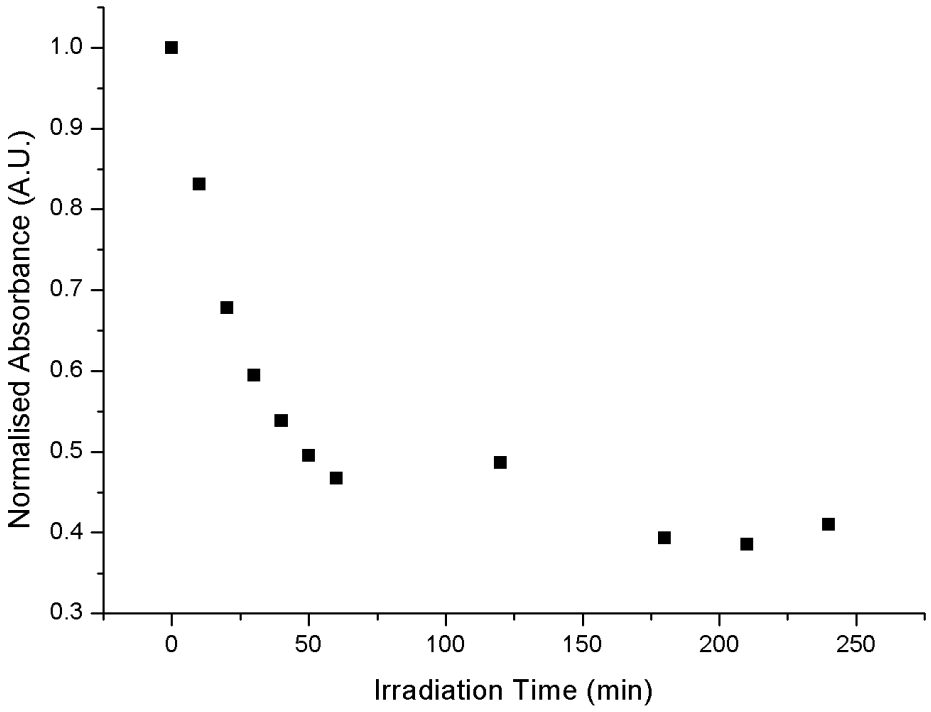


Figure 90 - Normalised Absorbance vs Time for Alpha-tocopherol (Run 1)

In both runs with α-tocopherol there is a very clear decrease in the absorbance at 294nm over the irradiation period with the overall change in the absorbance for run 1 being 40% and for run 2 64%. Out of all of the various antioxidants tested α-tocopherol shows the strongest case for the occurrence of chemical quenching.

The strong signs of chemical quenching from α-tocopherol are not too surprising since other studies have shown it have chemical reactions with singlet oxygen[82, 84].

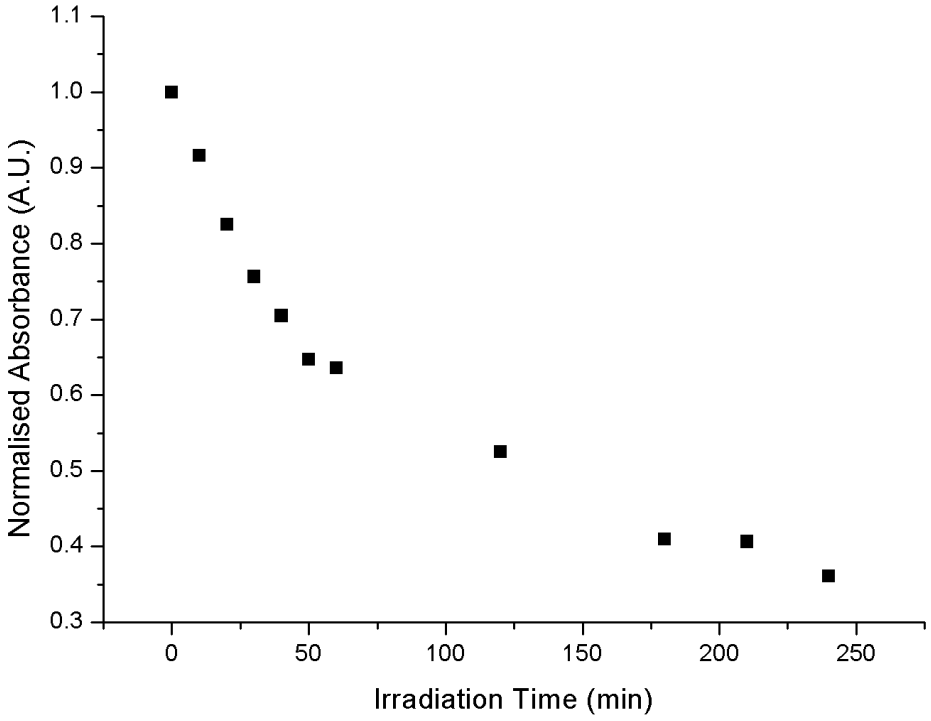


Figure 91 - Normalised Absorbance vs Time for Alpha-tocopherol (Run 2)

In both runs the most significant change in the absorbance occurs over the initial 50-minute period, after which the change in absorbance begins to lessen. This is most likely due to the reduction in the concentration of α-tocopherol within the solution meaning a lower probability of collisions with singlet oxygen and therefore a lower probability of reactions.

Figure 92 shows the plot of just the initial 50-minute period from the second run of α-tocopherol.

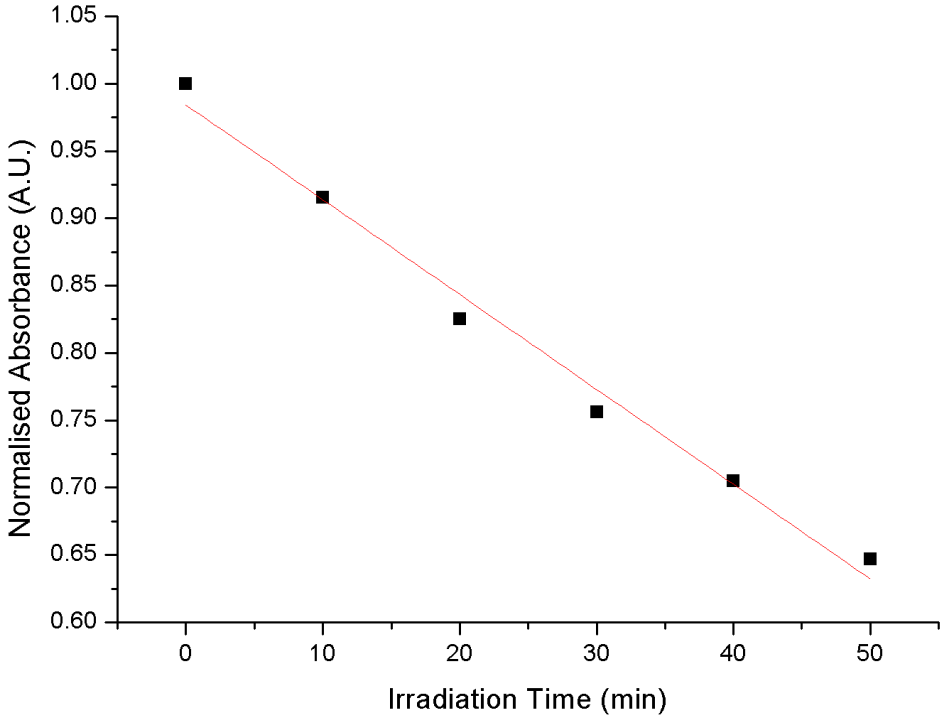


Figure 92 - Normalised Absorbance vs Time for Alpha-tocopherol (Run 2, First 50 min)

Table 53 - Results from Normalised Absorabnce vs Time for Alpha-tocopherol (Run2, First 50 min)

Adjusted R-square	0.98439
	Value
Intercept	0.9843
Slope	-0.00704 s^{-1}

Over the first 50 minute period the absorbance at 50 minutes of irradiation is 36% lower than the absorbance at the beginning of the run. The linear nature of the decrease over this time does suggest that this change in disappearance is due to a chemical reaction of the α-tocopherol with the singlet oxygen.

10. Results and Discussion V: Chromatography

Within this research attempts were made to utilise gas chromatography to attempt to discern if any of the antioxidants tested had a tendency to undergo chemical quenching as opposed to physical quenching. The theory was that by observing any changes in the chromatograms from before and after irradiation in the absence of a photosensitizer, used as a 'blank' measurement, as well as changes in the presence of a photosensitizer it would be possible to qualitatively state whether chemical changes, likely associated with chemical quenching, were occurring.

Unfortunately, due to unforeseen circumstances, the electronic copies of the spectra were lost. The spectra shown throughout the chapter were taken from the hard copy report print outs and as such limitations on the quality and capacity for manipulation of the spectra must be considered.

10.1. Individual Tests

10.1.1. Aminic

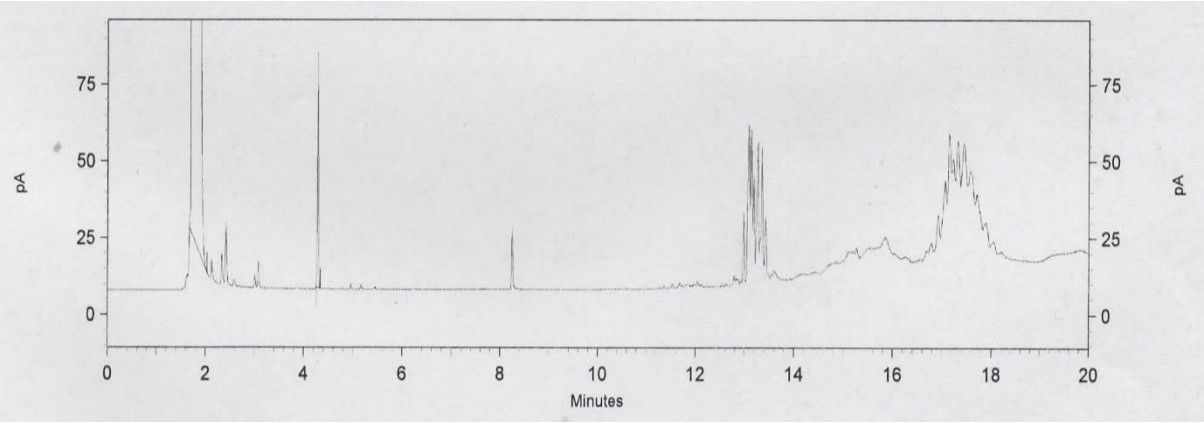


Figure 93 - Aminic at 5mg/ml

Initial tests run at a concentration of 5 mg/ml were most likely too low of a concentration to be properly detected by gas chromatography. However, visual analysis allowed for the discerning of peaks which can be associated with the aminic antioxidant, which are clusters of peaks around 13 to 13.5 minutes and another cluster of peaks around 17 to 17.5 minutes.

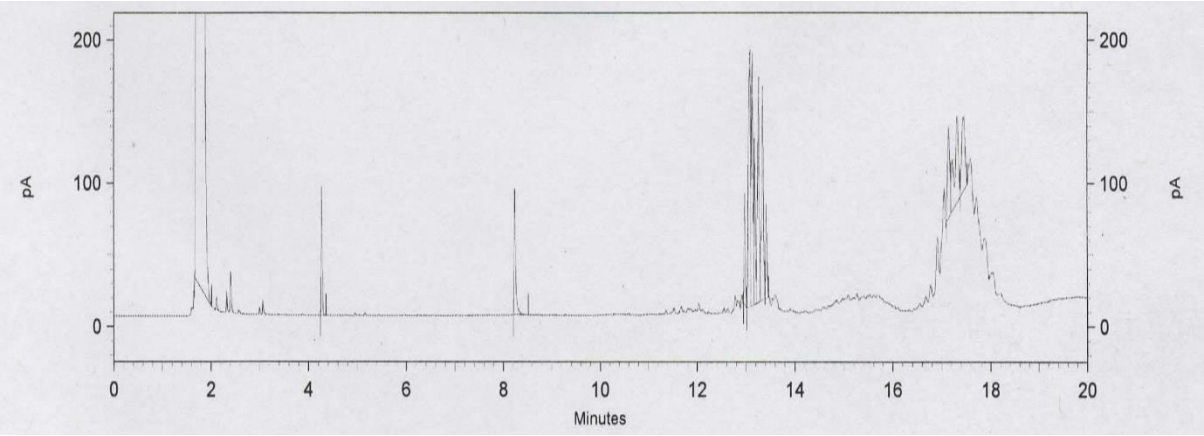


Figure 94 - Aminic at 15mg/ml

Running tests at 15 mg/ml instead clearly recorded these clusters of peaks which have been taken as the aminic antioxidant profile.

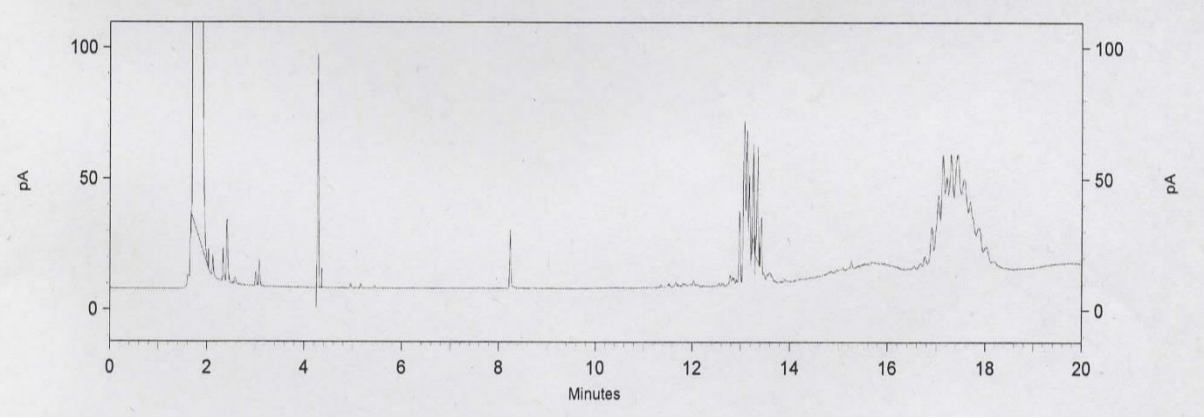


Figure 95 - Aminic 5mg/ml w/o Sensitizer, 25 min Irradiation

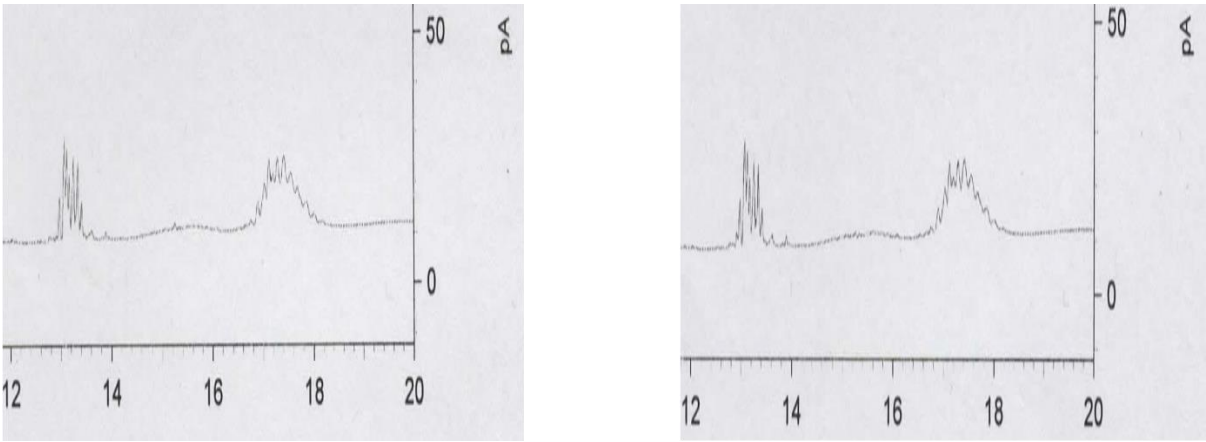


Figure 96 - Aminic 5mg/ml w/ Sensitizer ZnPh, Pre (left) and Post (right) 25 min Irradiation

After 25 minutes of irradiation for both concentrations without a sensitizer present there did not appear to be any significant deterioration of the aminic peaks. This was also the case with running the antioxidant, at 5 mg/ml, with two different sensitizers, methylene blue and zinc phthalocyanine.

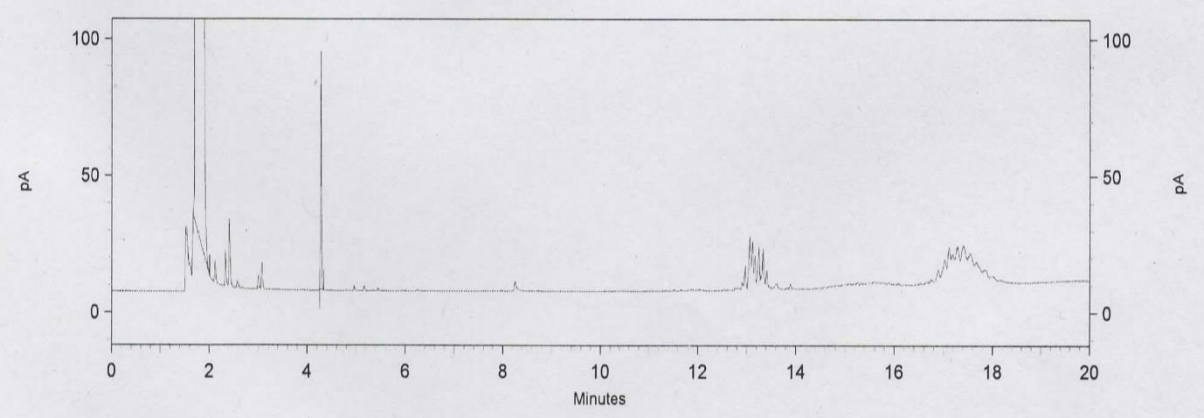


Figure 97 - Aminic 5mg/ml w/ Sensitizer MB, 25 min Irradiation

From the data that had been gathered, it does not appear that there is any significant deterioration of the aminic antioxidant under the irradiation conditions, nor any significant chemical quenching of singlet oxygen occurring.

10.1.2. Phenolic

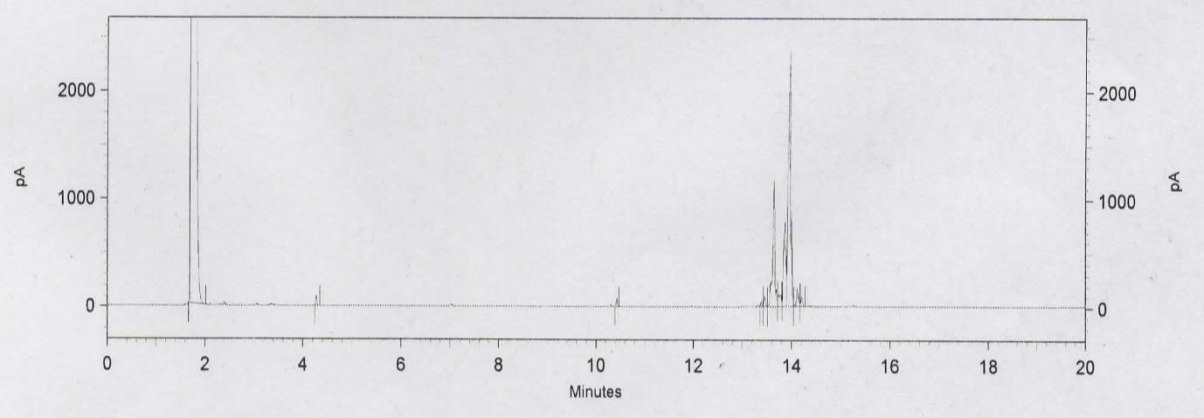


Figure 98 - Phenolic 25 mg/ml

The concentration of the phenolic antioxidant that was run gave a clear cluster of peaks between 13.3 and 14.3 minutes, with a strong peak around 13.9 minutes standing out in particular. This this was taken as the primary peak for the phenolic antioxidant for comparison before and after irradiation.

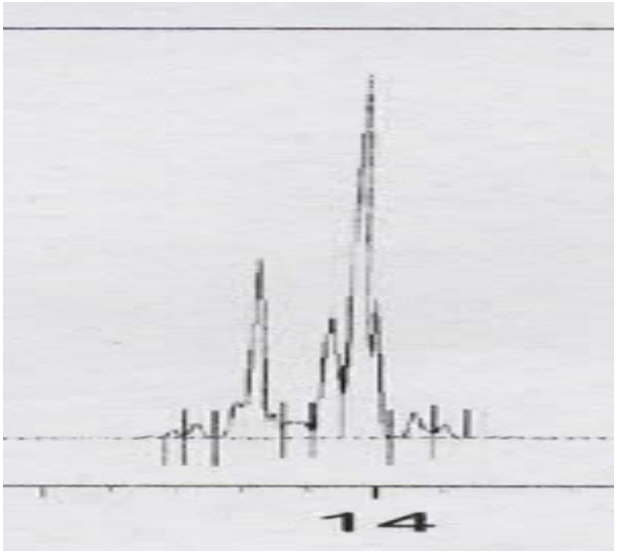


Figure 99 - Phenolic 25 mg/ml, Primary Peak

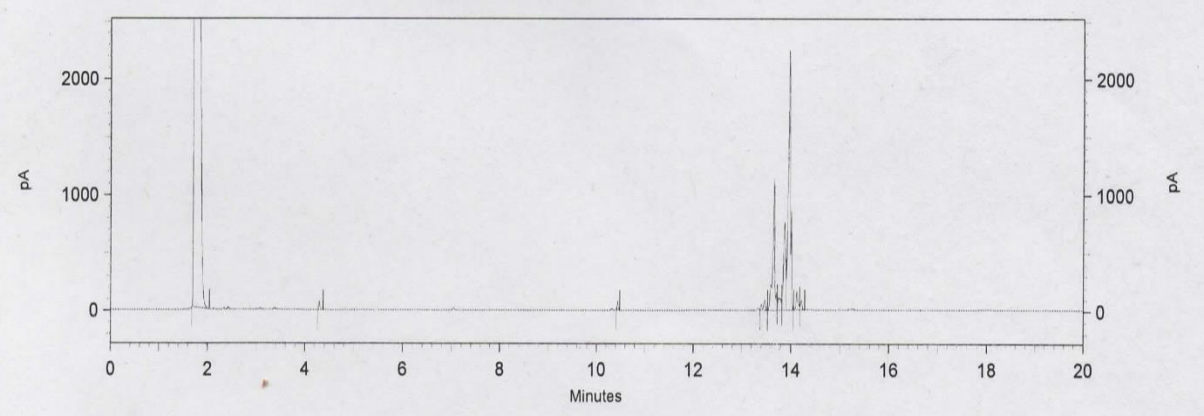


Figure 100 - Phenolic 25mg/ml w/o Sensitizer, 25 minute Irradiation

In the absence of a sensitizer there did not appear to be any significant changes in the peaks after a 25-minute irradiation period. This was also true after 25 minutes of irradiation with a singlet oxygen sensitizer present. However, after an hour of irradiation with the sensitizer a small peak began to emerge from the noise around 7 minutes.

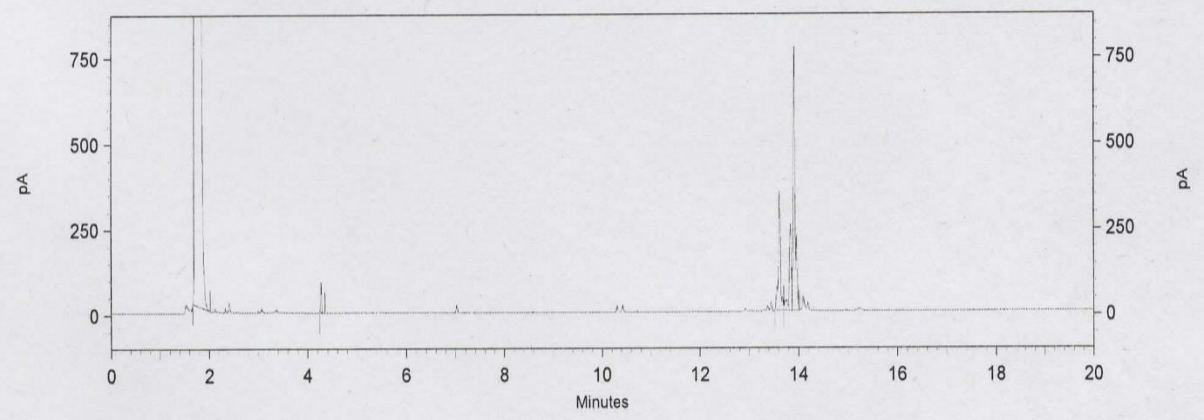


Figure 101 - Phenolic 25mg/ml w/ Sensitizer ZnPh, 25 minute Irradiation

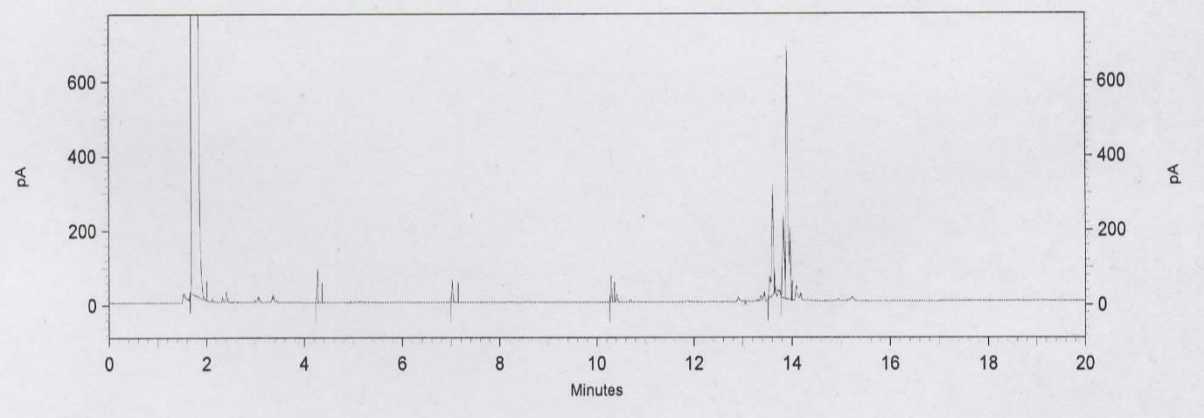


Figure 102 - Phenolic 25mg/ml w/ Sensitizer MB, 25 minute Irradiation

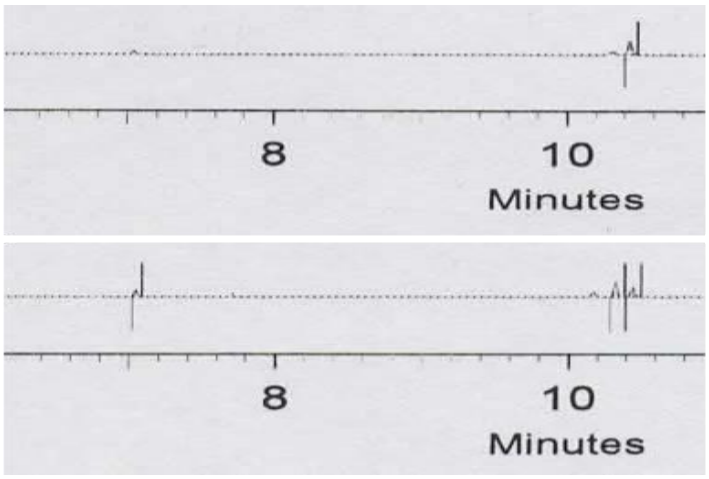


Figure 103 - Potential Appearance of New Peaks. Phenolic w/ MB Sensitizer, 25 min Irradiation

The appearance of a new peak could suggest the occurrence of chemical quenching of singlet oxygen, although given the peak is only just emerging after an hour as well as the lack of significant change in the phenolic peaks further testing would be required to confirm for certain that this is the case.

10.1.3. Sulfurized Olefin

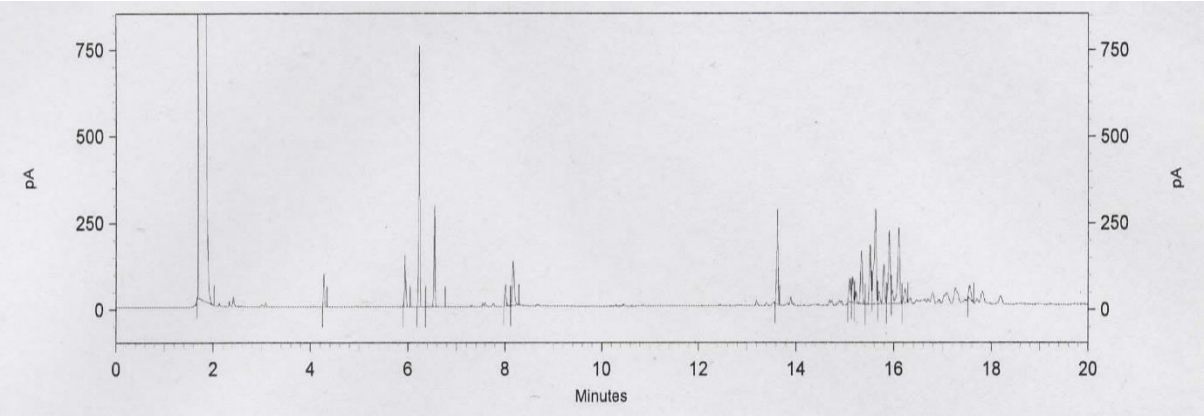


Figure 104 - Sulfurized Olefin 25mg/ml

As with the runs of the phenolic antioxidant the concentration of the sulfurized olefin used was sufficient to allow for characterisation of various peaks associated with the antioxidant. This included a small cluster of peaks between 6.2 and 6.5 minutes, also around 13.6 minutes and a final, larger, cluster of peaks between 15 and 16.2 minutes.

The presence of so many peaks with this antioxidant is not too surprising since, as it has been stated previously, the sulfurized olefin is the antioxidant most likely to contain impurities, mostly in the form of not fully reacted products, out of the three Lubrizol antioxidants.

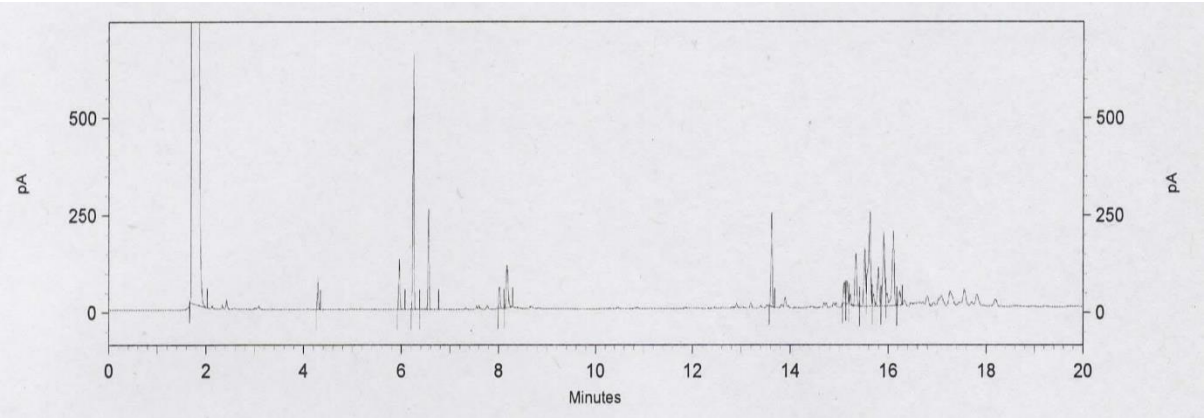


Figure 105 - Sulfurized Olefin 25mg/ml w/o Sensitizer, 25 minute Irradiation

After a 25-minute irradiation period, in the absence of a sensitizer, there did not appear to be any significant changes in the peaks. However, in two of the tree runs conducted with a sensitizer there were some changes observed, namely decreases in peaks between 15.3 and 15.6 minutes as well as some decreases post 16 minutes.

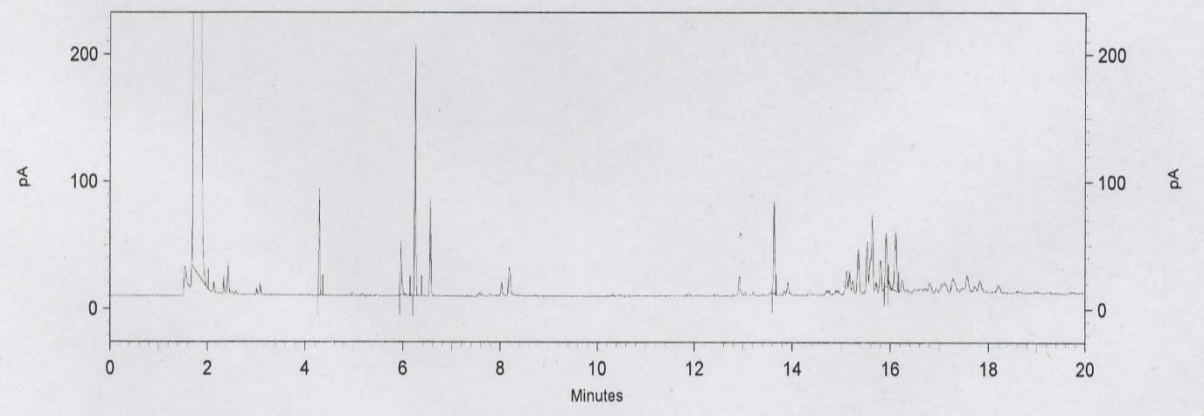


Figure 106 - Sulfurized Olefin 25mg/ml w/ Sensitizer ZnPh, 25 minute Irradiation

This became even more apparent when the irradiation time was increased to an hour long. Post one hour irradiation there was a clear drop in the peaks after the 15-minute mark. This information would strongly suggest that some chemical quenching is occurring with the sulfurized olefin antioxidant.

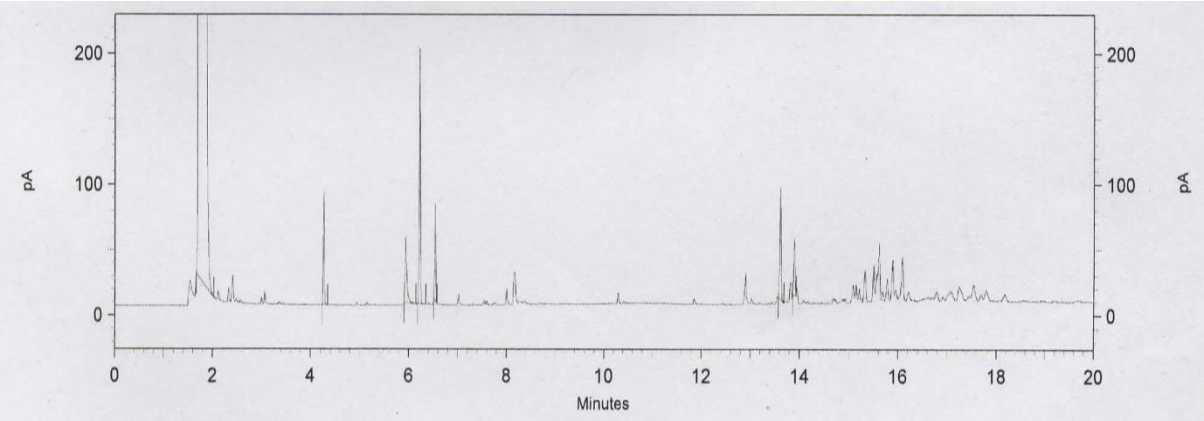


Figure 107 - Sulfurized Olefin 25mg/ml w/ Sensitizer ZnPh, 1 hour Irradiation

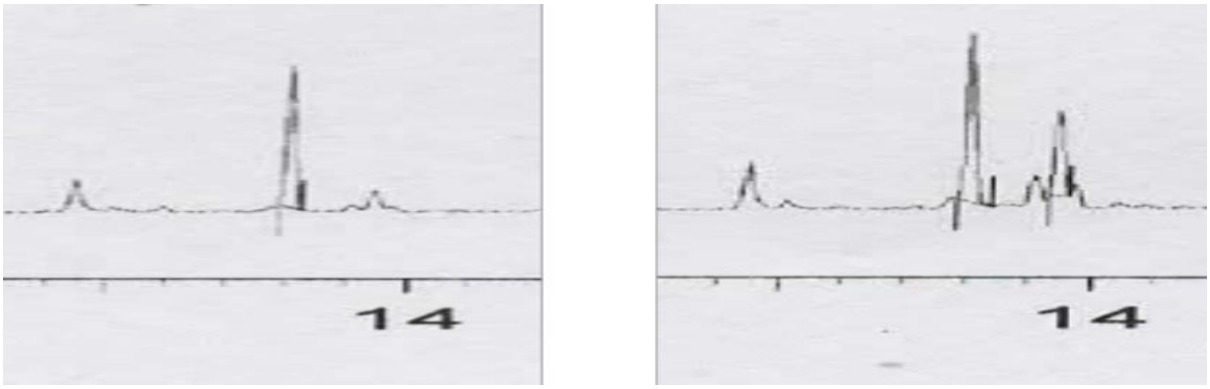


Figure 108 - Sulfurized Olefin 25mg/ml w/ Sensitizer ZnPh, 1 hour Irradiation. Closer look.

10.1.4. Squalene

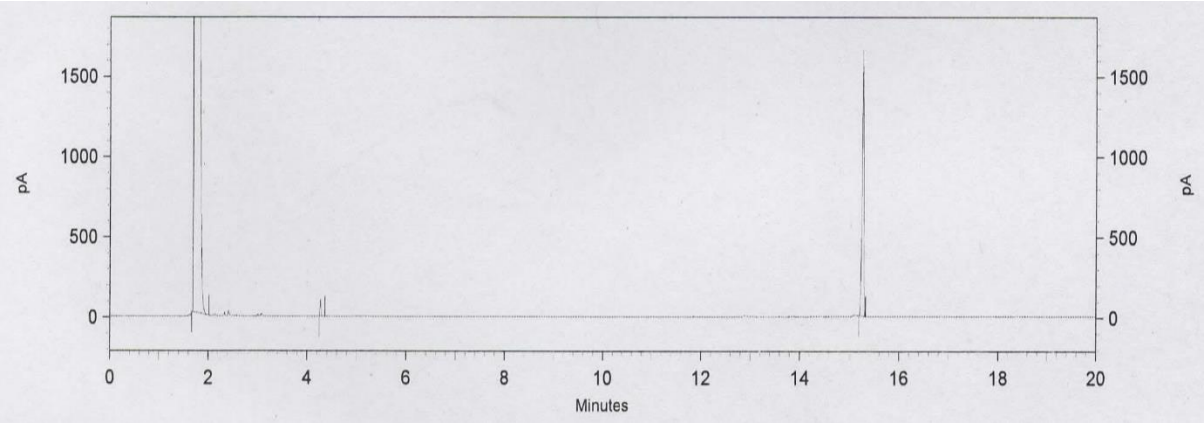


Figure 109 - Squalene 5mg/ml

At a concentration of 5 mg/ml there was a clear and well defined peak on the chromatogram at around 15.2 minutes. This compared with the chromatograms that have been seen previously for the Lubrizol antioxidants is significantly sharper and clearer, which attests to the difference in purity between the antioxidants.

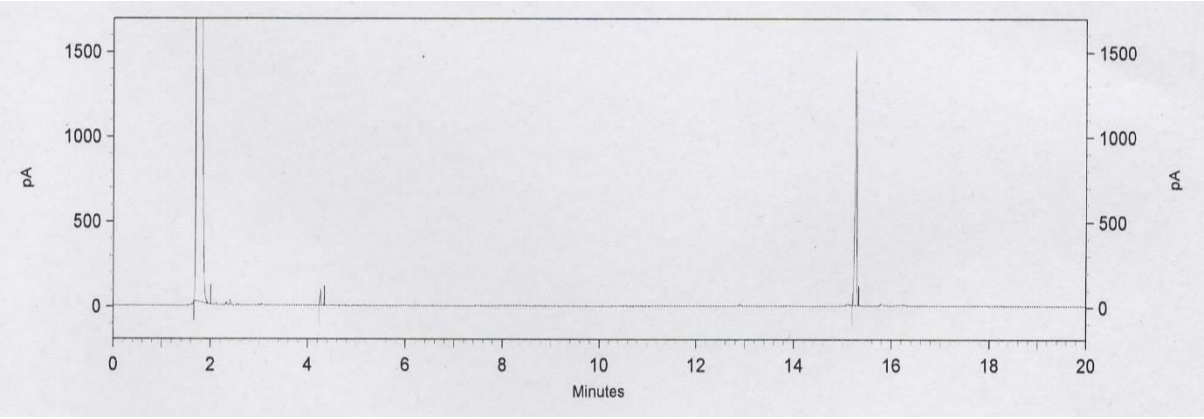


Figure 110 - Squalene 5mg/ml w/o Sensitizer, 1 hour Irradiation

After an hour of irradiation without a sensitizer present there did appear to be some degradation of the peak, suggesting that there may be some deterioration of the squalene antioxidant under the irradiation conditions. This also occurred after an hour of irradiation in the presence of a sensitizer. However, the lack of any new peaks emerging does not suggest any new product formation occurring which would be expected if the was any chemical quenching of singlet oxygen.

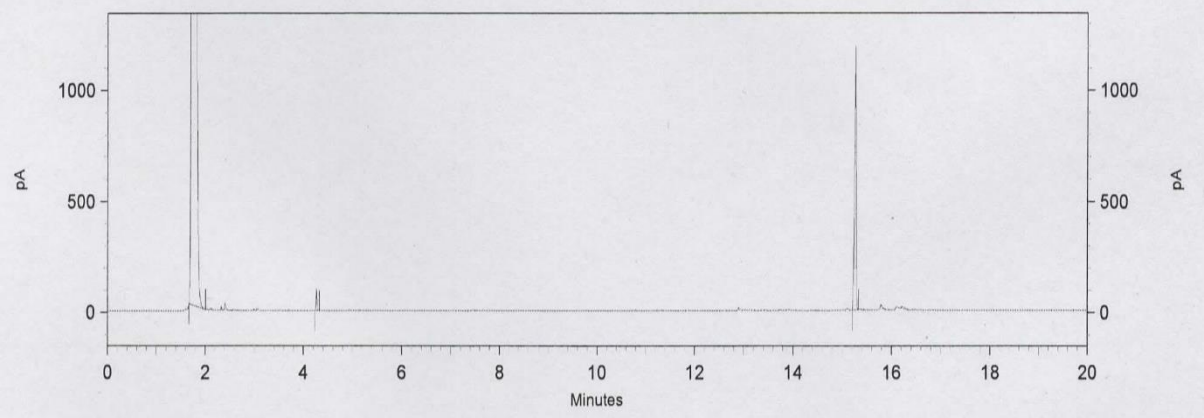


Figure 111 - Squalene 5mg/ml w/ Sensitizer ZnPh, 1 hour Irradiation

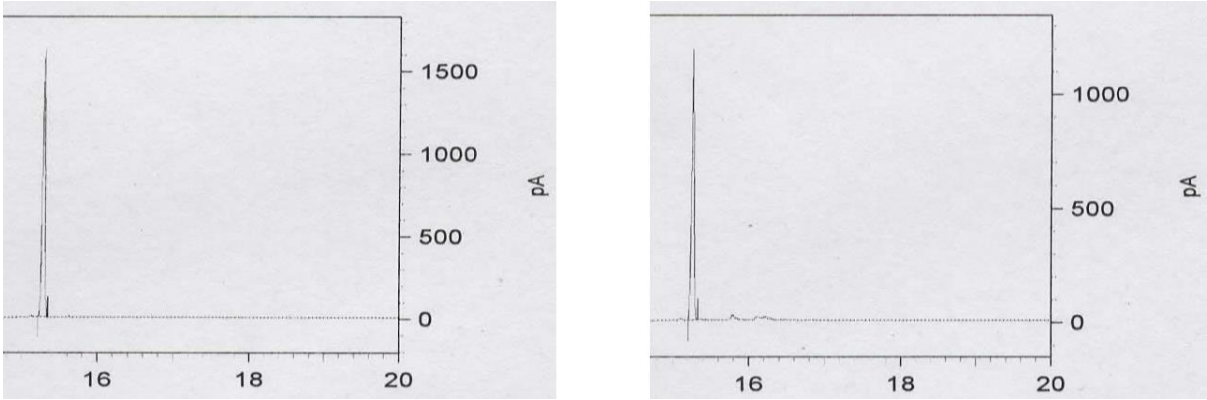


Figure 112 - Squalene 5mg/ml w/o and w/ Sensitizer ZnPh, 1 hour Irradiation

10.1.5. α-Tocopherol

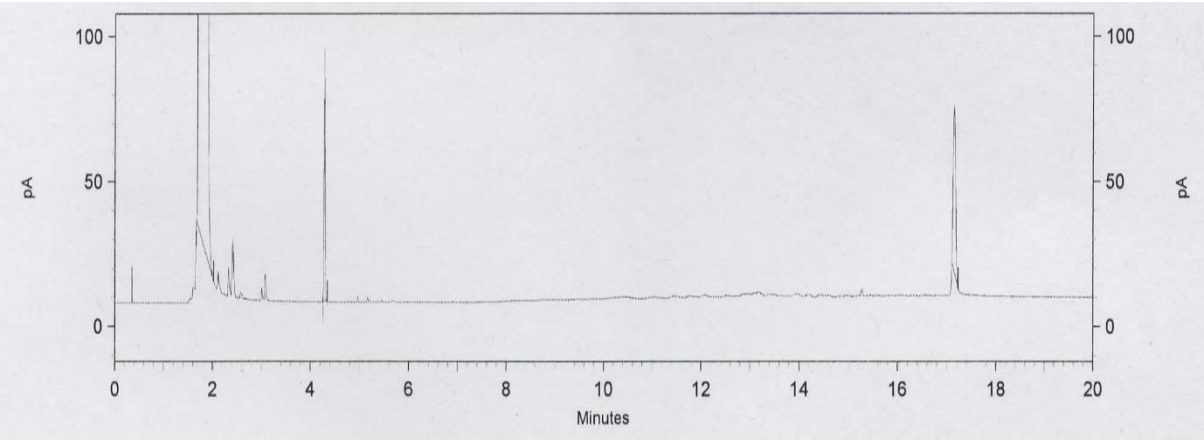


Figure 113 - α-Tocopherol 0.6mg/ml

Again, as with squalene, α-tocopherol at a concentration of 0.6 mg/ml had a very clear peak, especially when compared to the Lubrizol antioxidants, at around 17.1 minutes. After an hour

of irradiation without a sensitizer there did not appear to be any significant change in this peak. The irradiation with the sensitizer used a concentration of 0.5 mg/ml for α-tocopherol, which did not affect the quality of the peak seen.

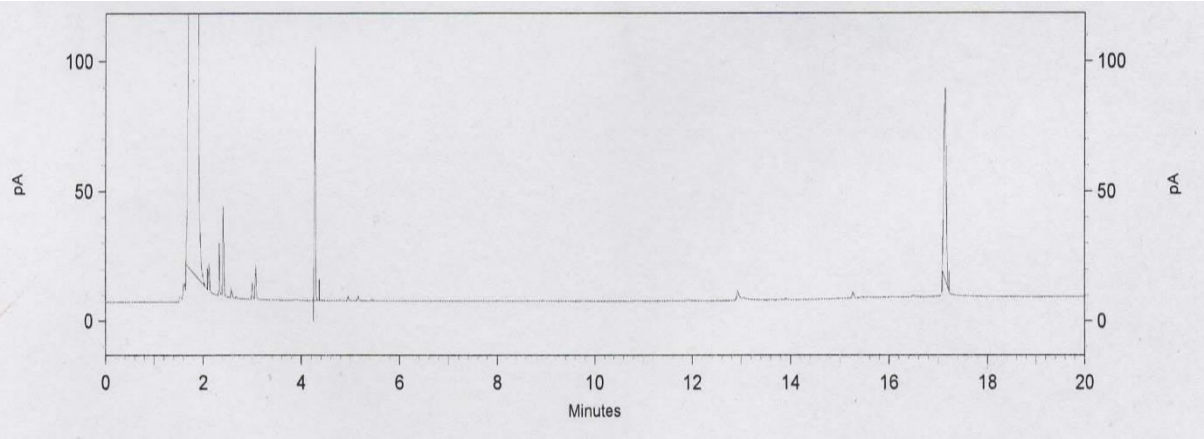


Figure 114 - α-Tocopherol 0.5mg/ml w/o Sensitizer, 1 hour Irradiation

After the hour long irradiation period there was a very significant decrease in the α-tocopherol peak to the point where, while the peak was still visually present, the height and area were not enough to be measured by the instrument. Visually a potential new peak also began to emerge from the noise around 15.2 minutes which could suggest product formation.

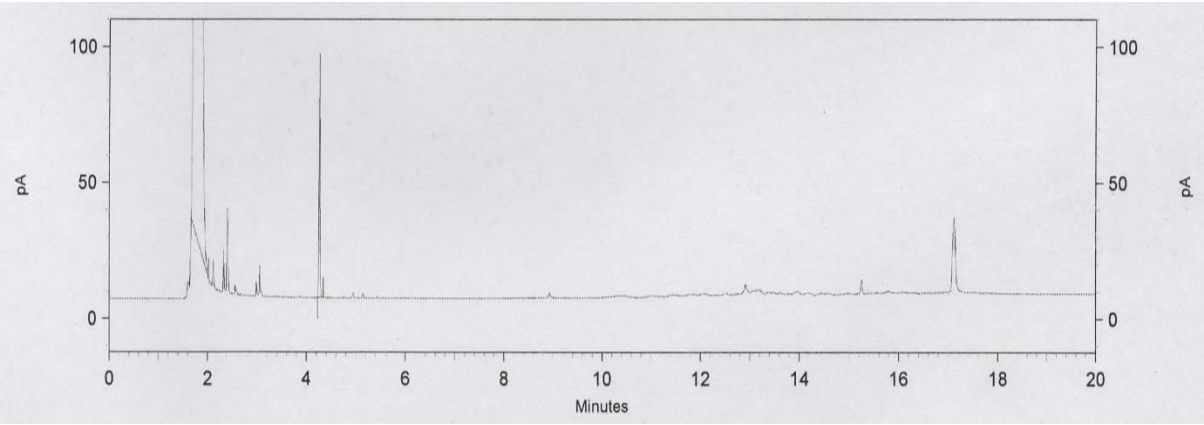


Figure 115 - α-tocopherol 0.5mg/ml w/ Sensitizer ZnPh, 1 hour Irradiation

If α-tocopherol is indeed chemical quenching singlet oxygen, then this could explain why there is such a significant drop off in the peak for α-tocopherol. However, it should also be noted that α-tocopherol is known to degrade slightly at room temperature, and as such this could also be attributing to the decrease in the peak if there is significant enough heat radiation occurring from the irradiation source.

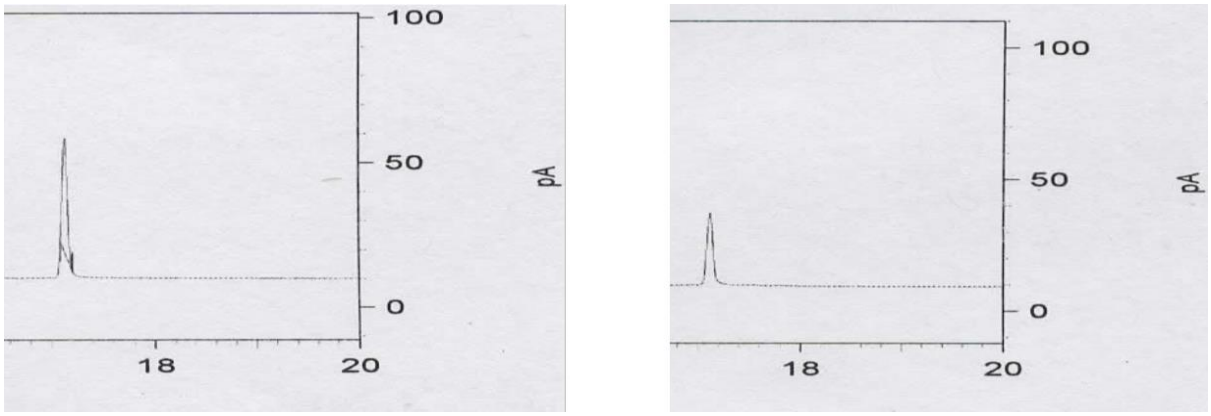


Figure 116 - α-tocopherol 0.5mg/ml w/ Sensitizer ZnPh, 1 hour Irradiation. Closer look.

10.2. Combination Tests

10.2.1. Aminic/Phenolic

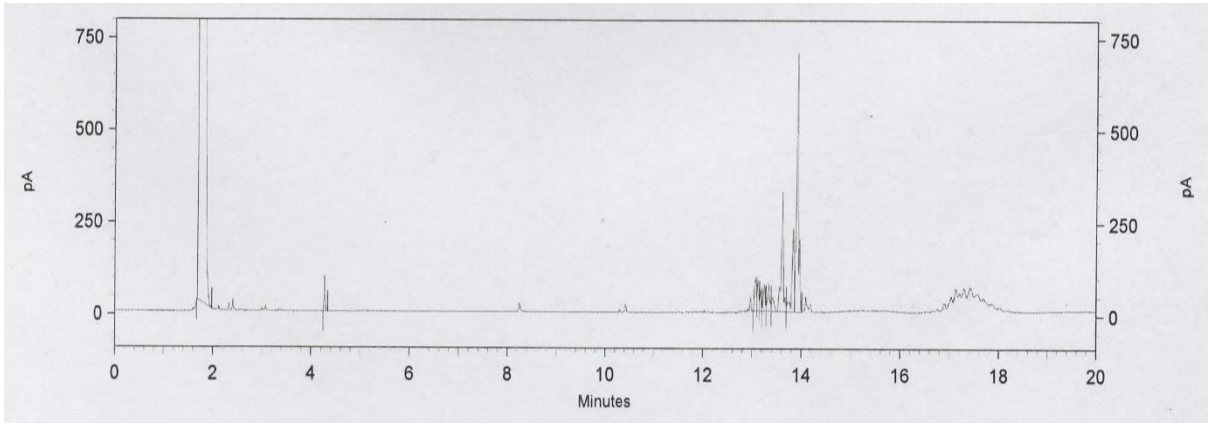


Figure 117 - Aminic/Phenolic (50:50)

The primary issue found from running the combination of the aminic and phenolic antioxidants with the method used was the separation of the peaks associated with the two since both of the main clusters of peaks fall within the range of 13 to 14 minutes.

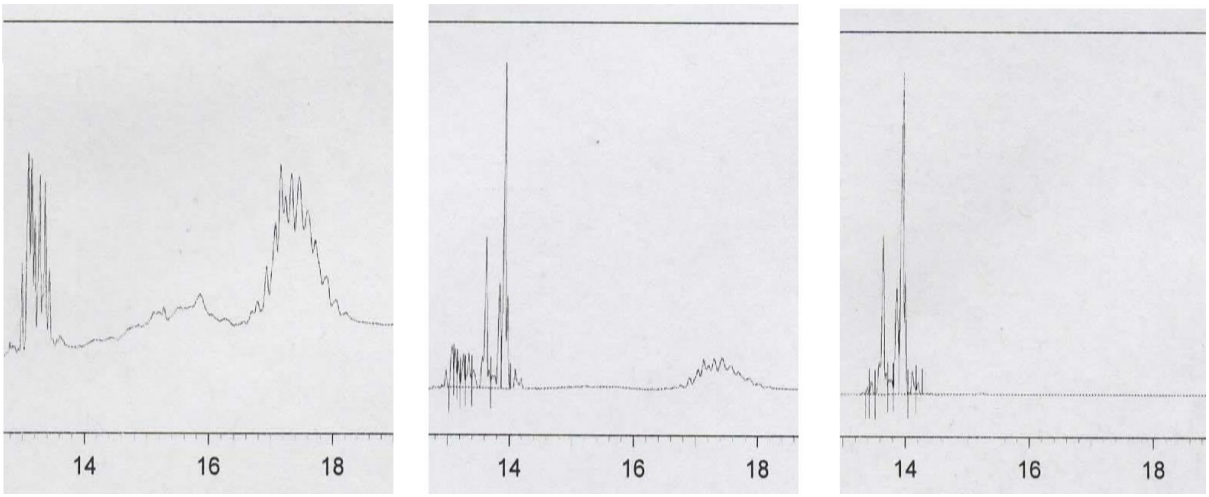


Figure 118 - Comparison of Peaks. Aminic alone (left), Combined (mid), Phenolic alone (right)

The main peak of the phenolic antioxidant, which lies around 13.9 minutes, is clear and defined from the rest of the peaks and lies outside of the previously recorded range of the aminic which means that it is only affected by changes in the phenolic antioxidant. The main peak which can be taken from the cluster of peaks associated with the aminic antioxidant lies around 13.1 minutes. However, it is not as clearly defined from the cluster of peaks as the main phenolic peak is.

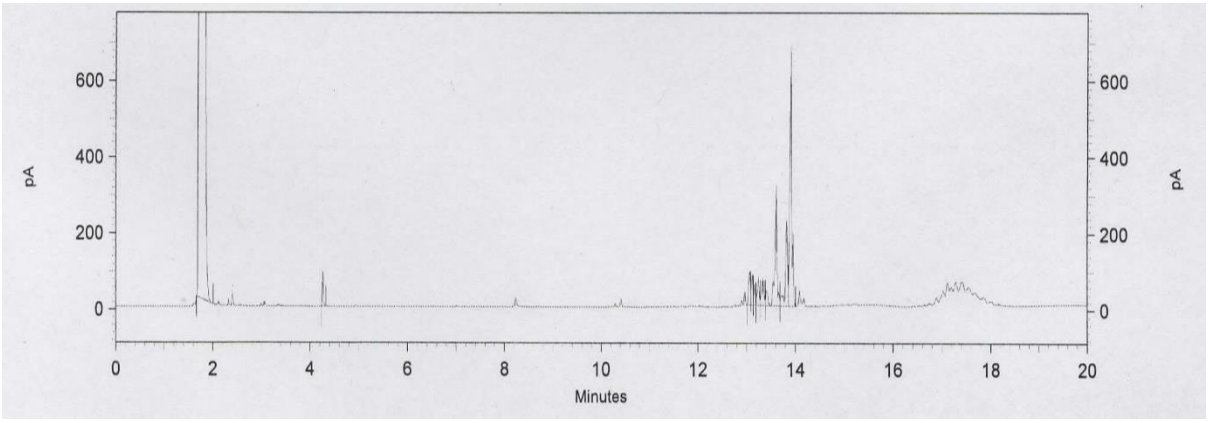


Figure 119 - Aminic/Phenolic (50:50) w/o Sensitizer, 1 hour Irradiation

Post a 1 hour irradiation period, in the absence of a sensitizer, showed no significant changes in the main peaks for both antioxidants. This was also the case with the runs post-irradiation period in the presence of a sensitizer, with no significant changes to either of the peaks.

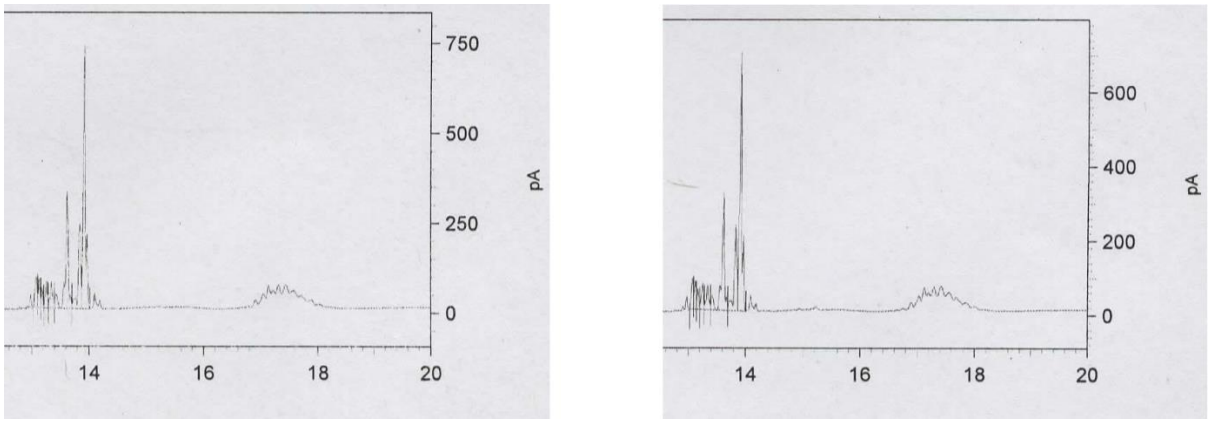


Figure 120 - Aminic/Phenolic (50:50) w/ Sensitizer, 1 hour Irradiation

This information also fits with what was seen in the individual tests for the aminic antioxidant. However, there was not as noticeable change in the phenolic peak as there was in the individual tests, which could be due to a lesser strain being placed on the phenolic antioxidant to quench singlet oxygen due to the combination with the aminic antioxidant.

10.2.2. Aminic/Sulfurized Olefin

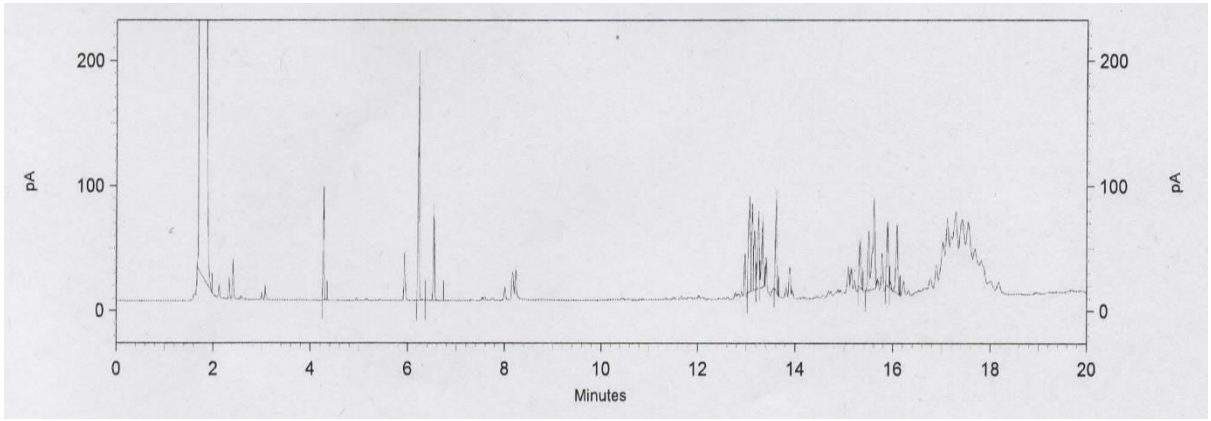


Figure 121 - Aminic/Sulfurized Olefin (50:50)

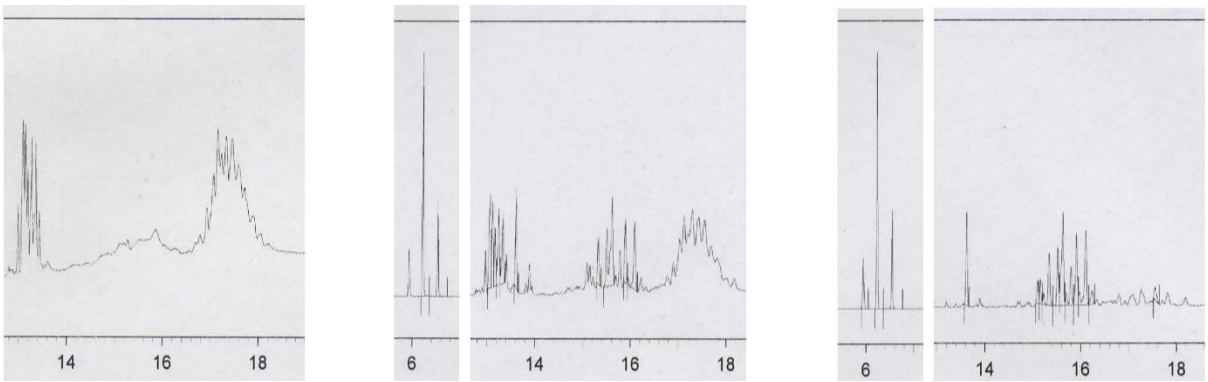


Figure 122 - Comparison of Peaks. Aminic (left), Combined (mid), Sulfurized Olefin (right)

Unlike with the combination of the aminic and phenolic antioxidants, there was no cross over of the peak clusters with the aminic and sulfurized olefin. Here the peak clusters that were seen in the individual antioxidant runs were clearly seen and separate on the chromatogram, although the peak areas are relatively small which could be an issue in attempting to discern changes.

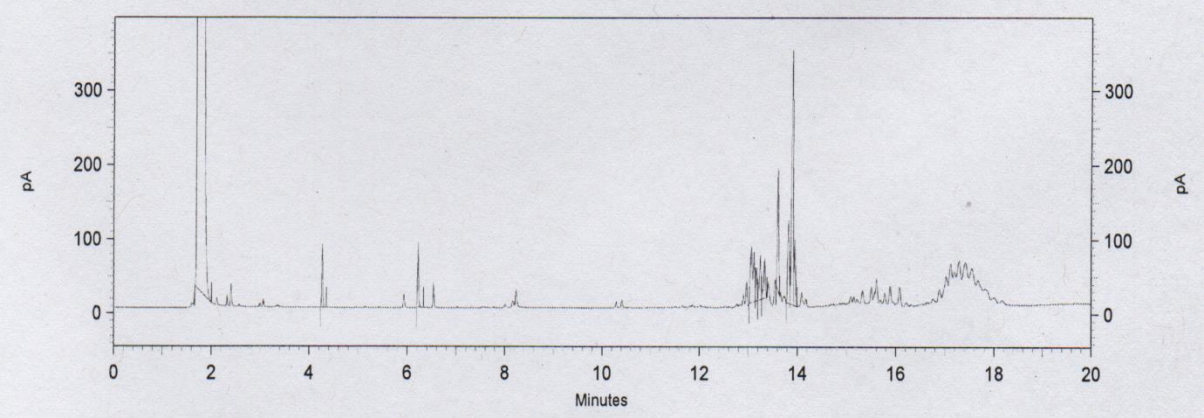


Figure 123 - Aminic/Sulfurized Olefin (50:50) w/o Sensitizer, post 1 hour Irradiation

Post an hour long irradiation without a sensitizer showed significant decreases in the sulfurized olefin peaks to the point that they were almost to the point of the noise. This was concerning since in the individual tests in the absence of a sensitizer there did not appear to be any significant changes in the peaks for the sulfurized olefin. It is especially concerning since this was not apparent within the runs containing a sensitizer post irradiation; instead there was no significant changes in the peaks for either of the antioxidants found.

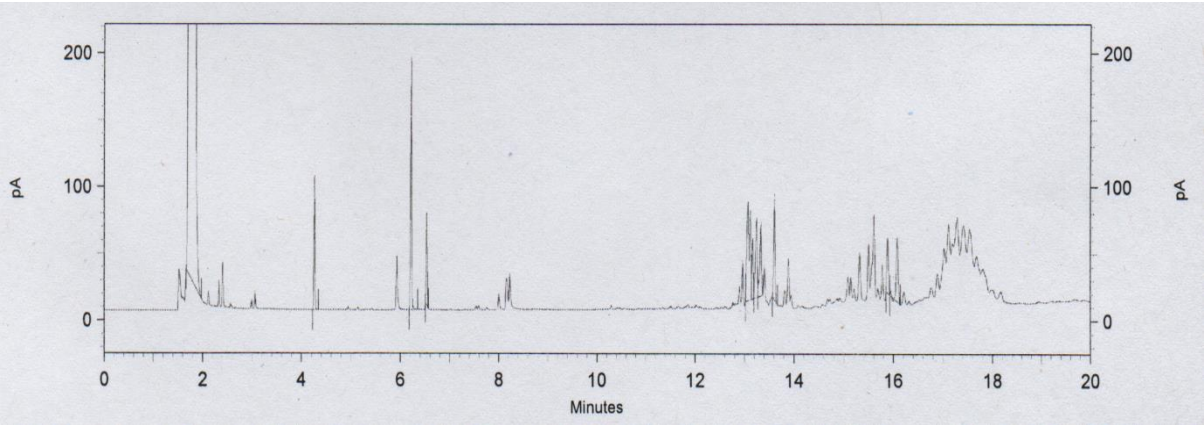


Figure 124- Aminic/Sulfurized Olefin (50:50) w/ Sensitizer ZnPh, 1 hour Irradiation

Therefore, either there was contamination of the samples or there is very significant reaction occurring between the aminic and sulfurized olefin, although since there was no significant change in the aminic peaks this is unlikely to be true. Either way further testing would require

acquiring another data set for these conditions to determine the accuracy of these previous findings.

10.2.3. Aminic/Squalene

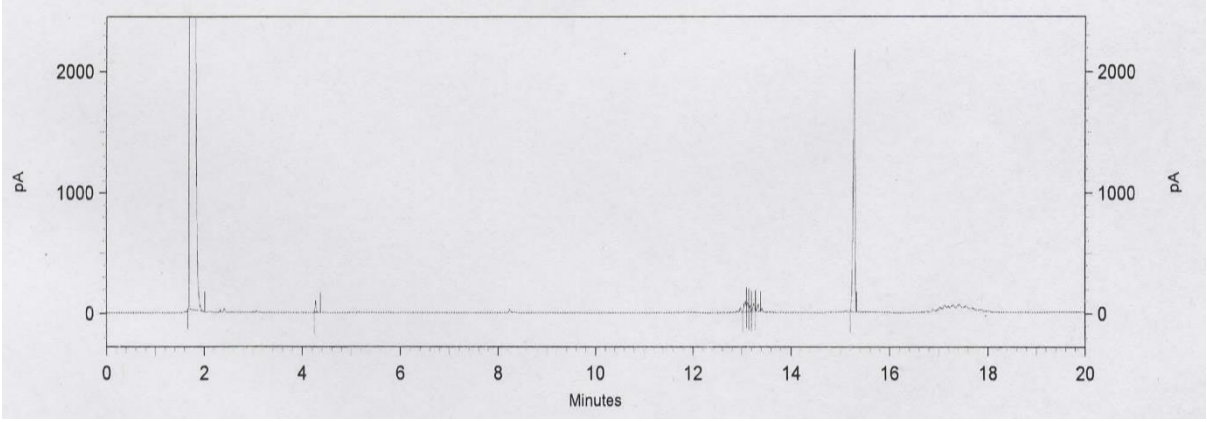


Figure 125 - Aminic/Squalene (50:50)

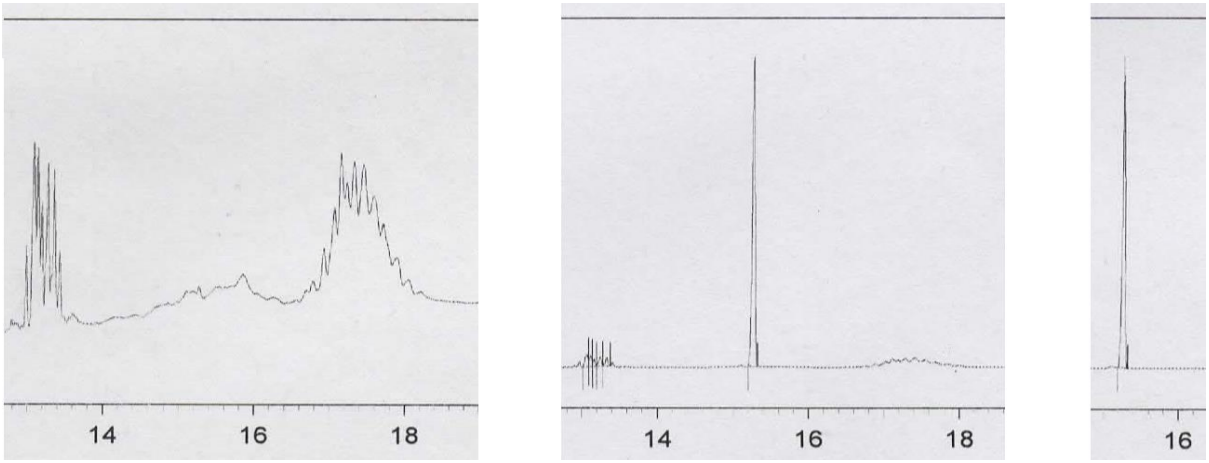


Figure 126 - Comparison of Peaks. Aminic (left), Combined (mid), Squalene (right)

Once again issues with the measurement of the cluster of peaks associated with the aminic antioxidant were apparent, most likely made more so by the clear, sharp squalene peak also seen within the mixture. This makes it hard to truly determine any changes in the aminic peaks.

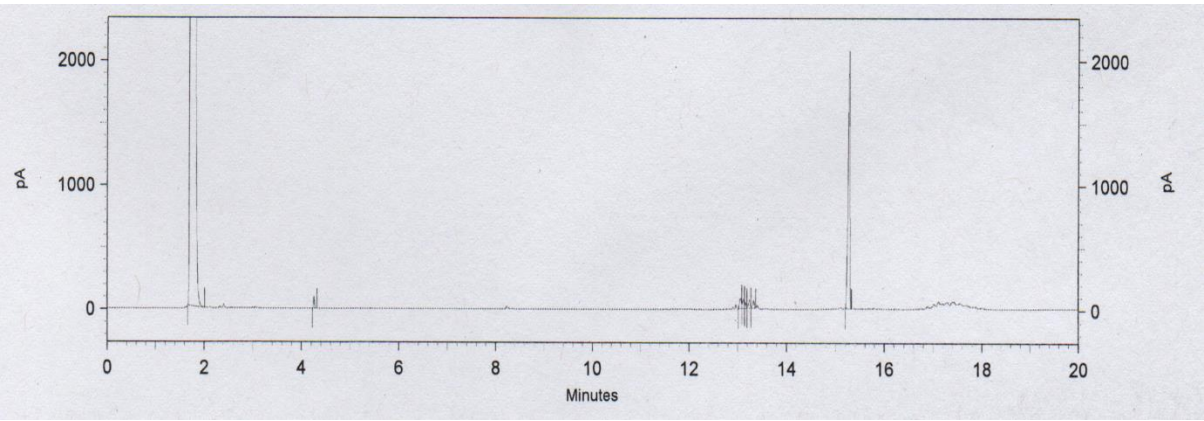


Figure 127 - Aminic/Squalene (50:50) w/o Sensitizer, 1 hour Irradiation

Post one hour irradiation, in the absence of a sensitizer, there was not any significant change in the antioxidant peaks. However, after the irradiation period with a sensitizer present, there was a noticeable decrease in the squalene peak, but no significant change in the aminic peaks.

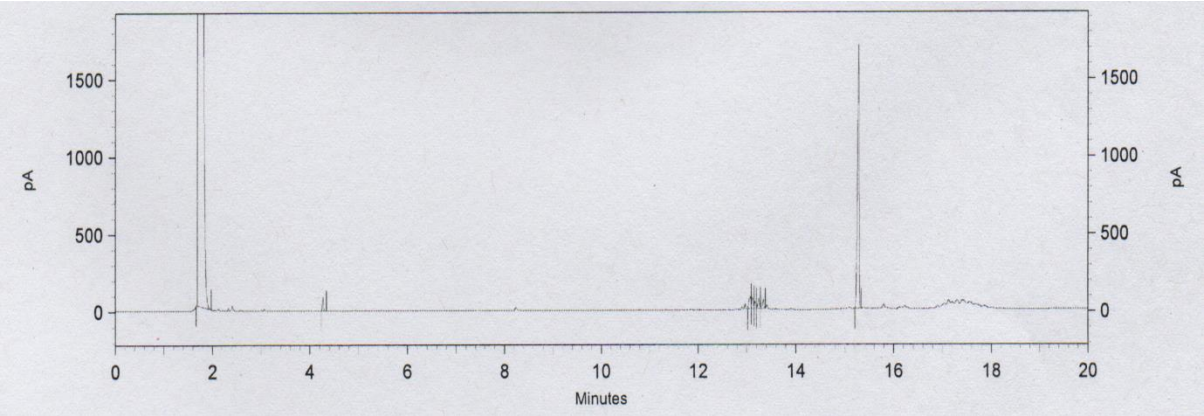


Figure 128 - Aminic/Squalene (50:50) w/ Sensitizer ZnPh, 1 hour Irradiation

There was also the potential emergence of a new peak after the squalene peak on the chromatogram which could potentially be product formation occurring. However, as has been stated earlier, a longer irradiation period would be needed to confirm the significance of this.

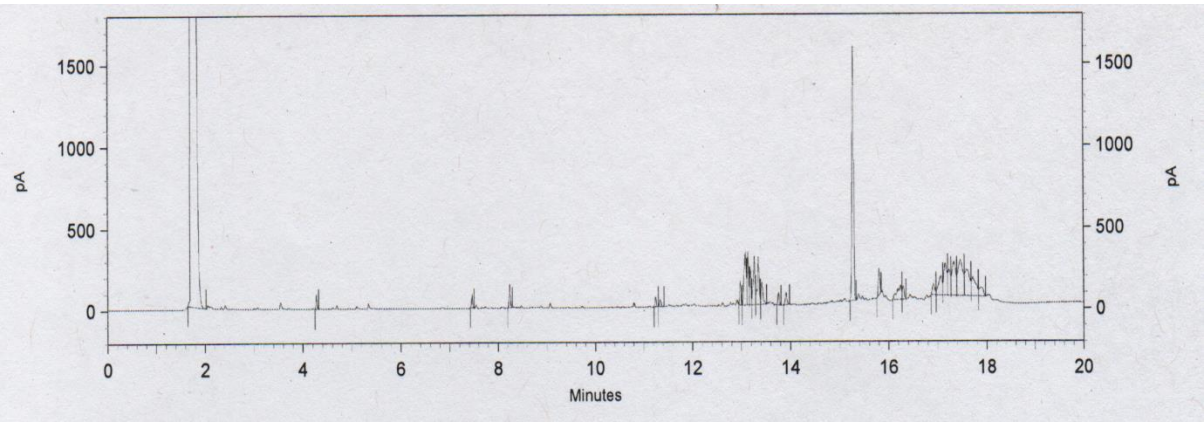


Figure 129 - Aminic/Squalene (50:50) w/ Sensitizer, 24 hour Irradiation

After irradiating for a 24 hour period the changes were indeed far more pronounced, with a very significant drop in the squalene peak and some slight changes in the later aminic cluster of peaks. However, the most interesting development was in the emergence of three new sets of peaks; one around 11.2 to 11.4 minutes, another around 13.7 to 14 minutes and a final one around 16.1 and 16.2 minutes. Given that all of these new peaks are not within the same ranges as any of the pre-existing antioxidant peaks the emergence of these peaks strongly hints at product formation as a result of reaction with squalene.

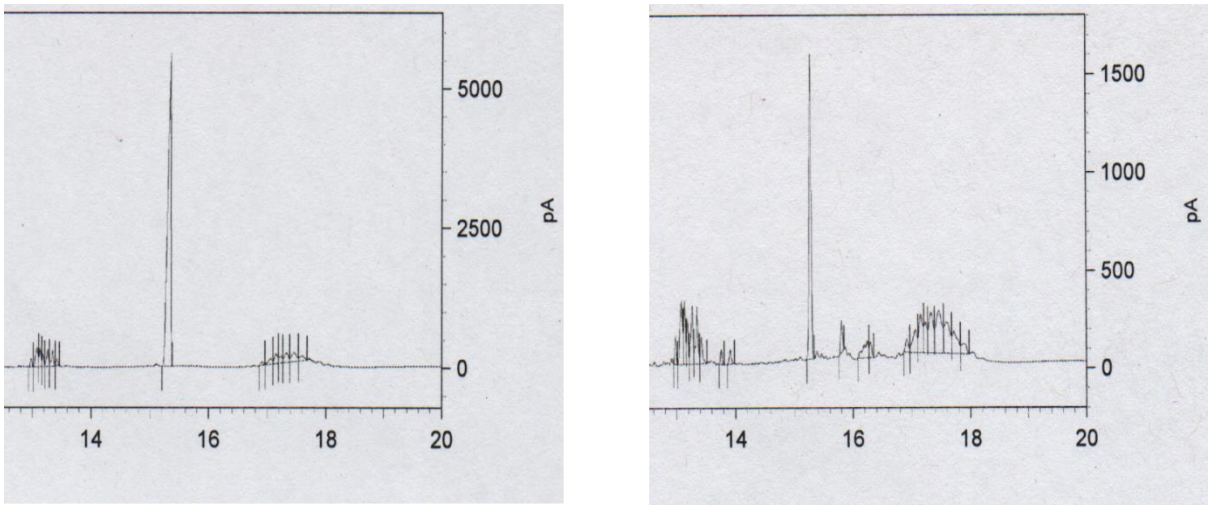


Figure 130 - Comparison of Aminic/Squalene Pre (left) and Post (right) 24 hour Irradiation w/ ZnPh Sensitizer

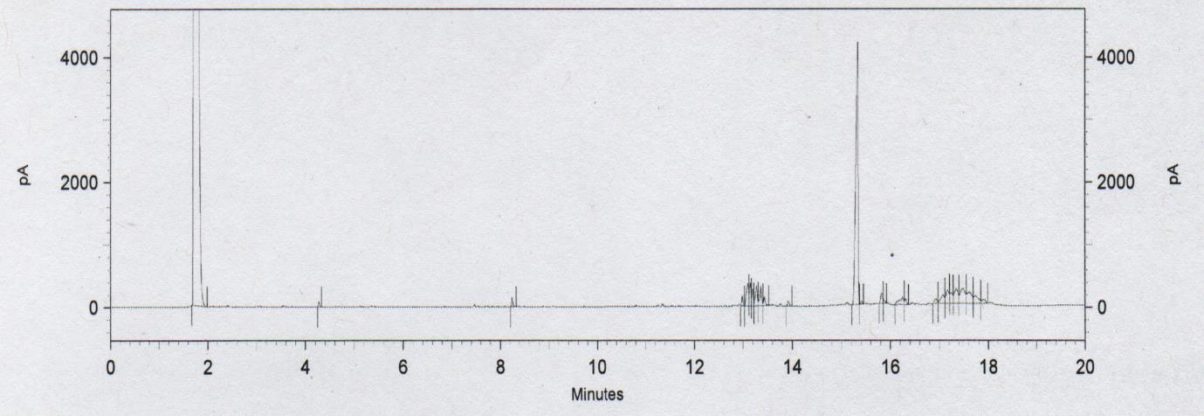


Figure 131 - Aminic/Squalene (50:50) w/o Sensitizer, 24 hour Irradiation

Tests were also run over a 24-hour irradiation period without a sensitizer present to confirm what changes were due to potential chemical quenching of singlet oxygen and what were not. From this a significant drop in the squalene peak was still seen, although not as large a drop as was seen in the presence of the sensitizer, as well as the emergence of new peaks around 14 minutes and 15.8 to 16.3 minutes which would suggest these peaks are not due to chemical quenching. The minor changes in the later aminic cluster of peaks that was seen in the sensitizer runs was again seen without the sensitizer.

Overall it would appear that there is at least some reaction occurring between the aminic antioxidant and squalene with the possible products showing up on the chromatogram at the new emerging peaks.

10.2.4. Phenolic/Sulfurized Olefin

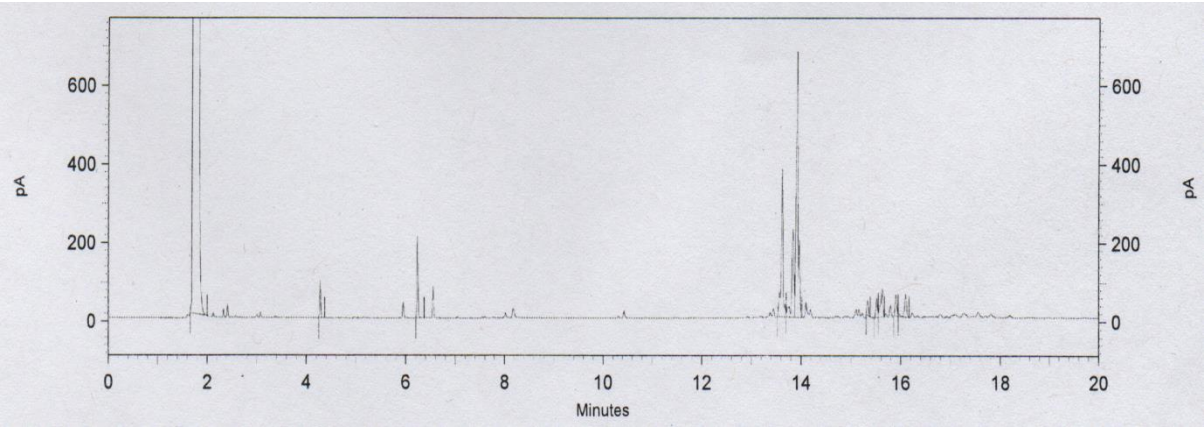


Figure 132 - Phenolic/Sulfurized Olefin (50:50)

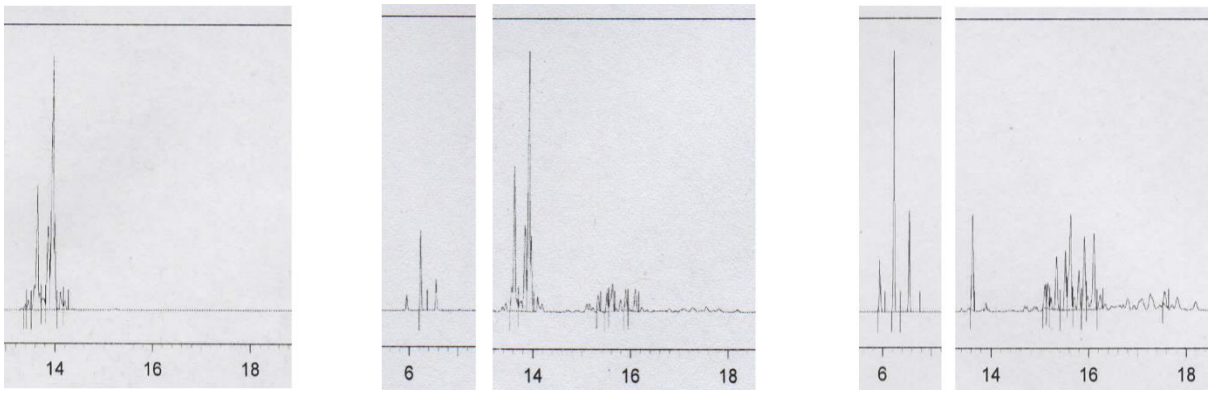


Figure 133 - Comparison of Peaks. Phenolic (left), Combined (mid), Sulfurized Olefin (right)

The phenolic and sulfurized olefin peaks that were seen in the individual testing were thankfully significantly separated enough to allow for discerning of said peaks within the chromatogram of the combined mixture. The primary phenolic peak was clear and distinct from the phenolic cluster, while the sulfurized olefin peaks were more level but the clusters still present.

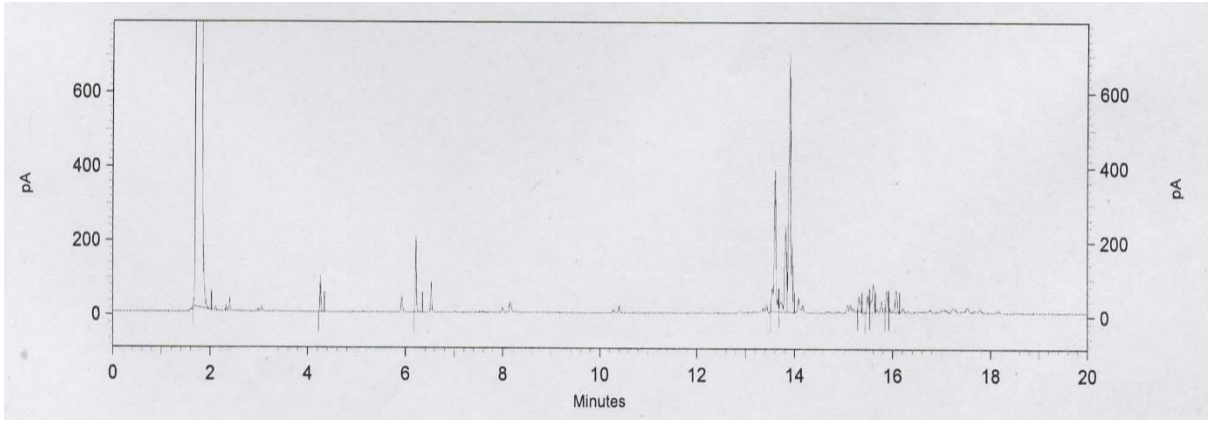


Figure 134 - Phenolic/Sulfurized Olefin (50:50) w/o Sensitizer, 1 hour Irradiation

Post an hour long irradiation without a sensitizer there were no significant changes to the peaks of the two antioxidants. However, in the presence of a sensitizer there was a slight decrease in the phenolic peak as well as the later sulfurized olefin cluster of peaks around 15 to 16 minutes. The sulfurized olefin peaks around 6.2 minutes did not appear to be significantly affected.

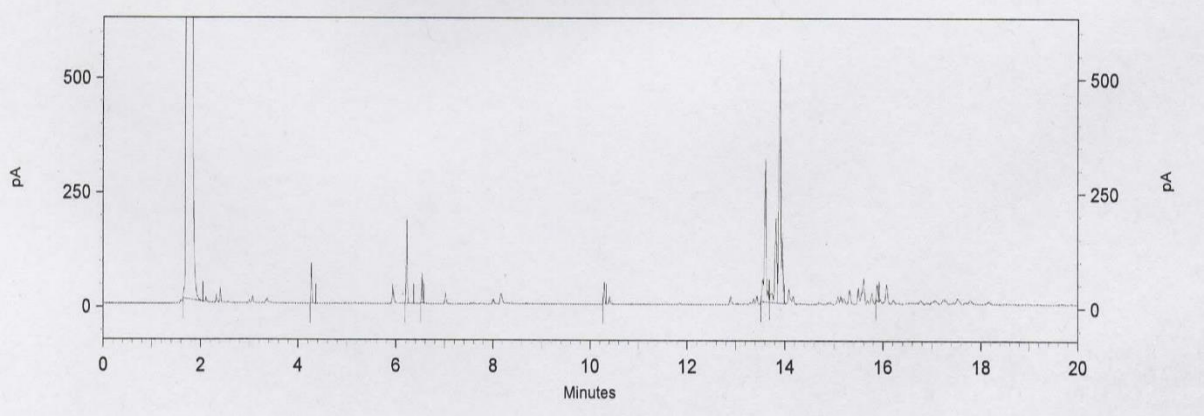


Figure 135 - Phenolic/Sulfurized Olefin (50:50) w/ Sensitizer ZnPh, 1 hour Irradiation

Since, as was noted in the individual tests, the sulfurized olefin has the highest probability for impurities in the form of partially reacted or unreacted components it would be of great interest to figure out what exactly each of the sulfurized olefin peaks is associated with. From that information, it would be possible to figure out if there is a reaction occurring between the phenolic antioxidant and what is currently presumed to be the 'pure' sulfurized olefin or if the reaction is in fact occurring with an impurity within the sample.

10.2.5. Phenolic/Squalene

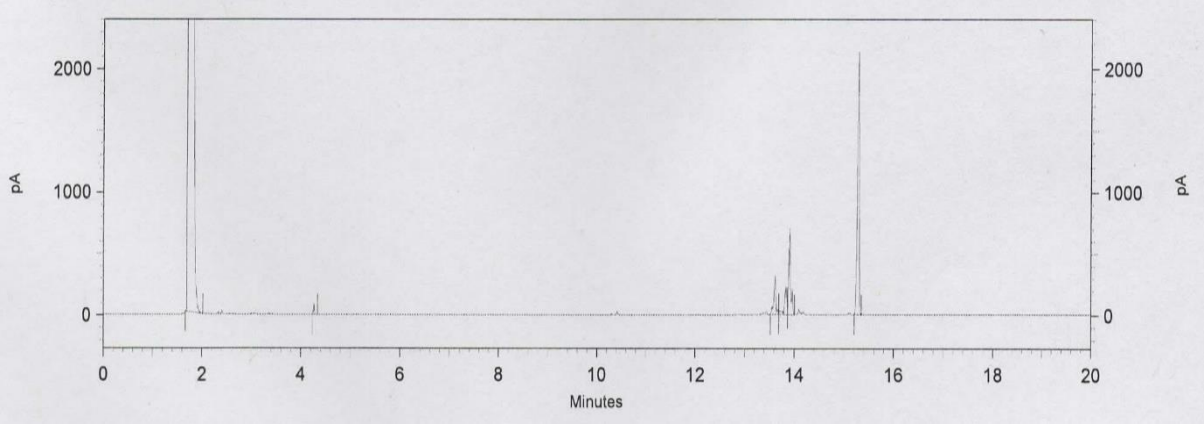


Figure 136 - Phenolic/Squalene (50:50)

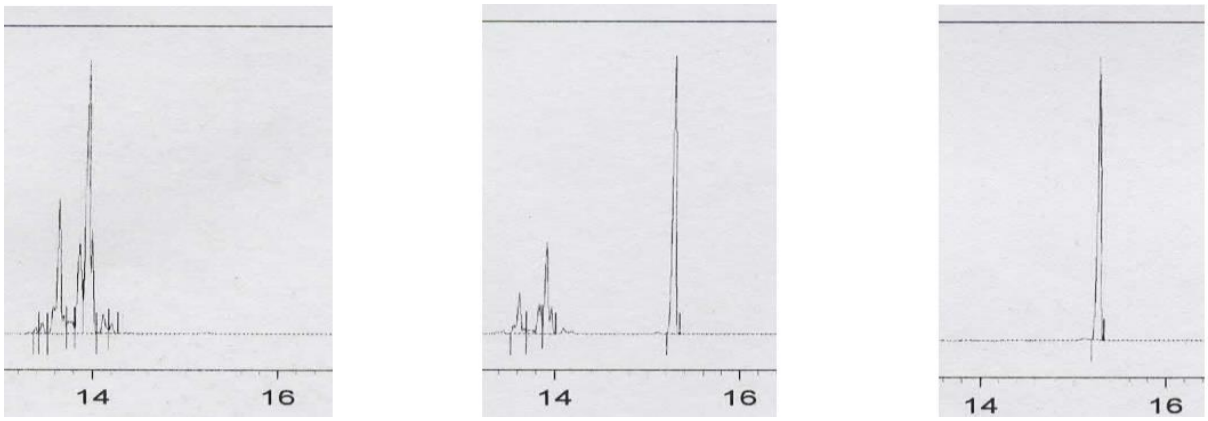


Figure 137 - Comparison of Peaks. Phenolic (right), Combined (mid), Squalene (right)

This combination probably had the clearest separation of peaks of all of the combinations of antioxidants discussed here, with clear peaks for both the phenolic antioxidant and squalene at the appropriate times for what was seen in the individual tests and no obvious crossover of the peak sets.

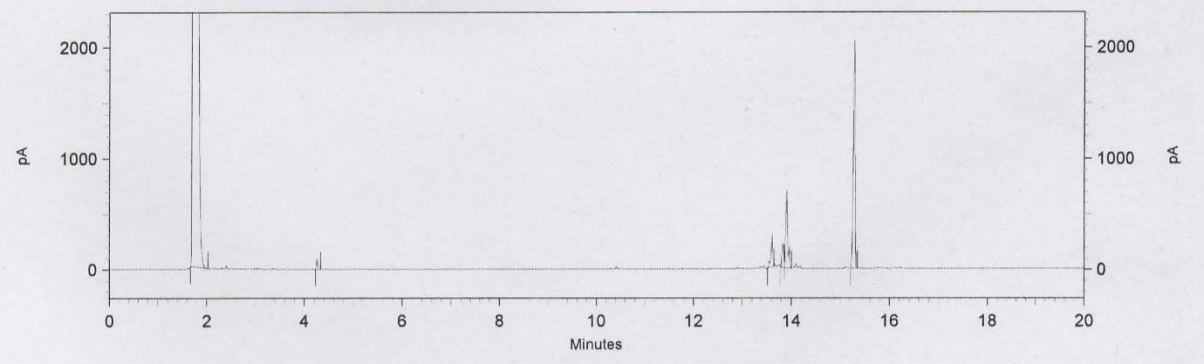


Figure 138 - Phenolic/Squalene (50:50) w/o Sensitizer, 1 hour Irradiation

Post a one hour irradiation period, in the absence of a sensitizer, a slight decrease in the phenolic peak was noted, while the squalene peak showed no significant change. However, this observation was reversed for the runs containing the sensitizer; where a decrease in the squalene peak was observed while the phenolic peaks showed no significant change.

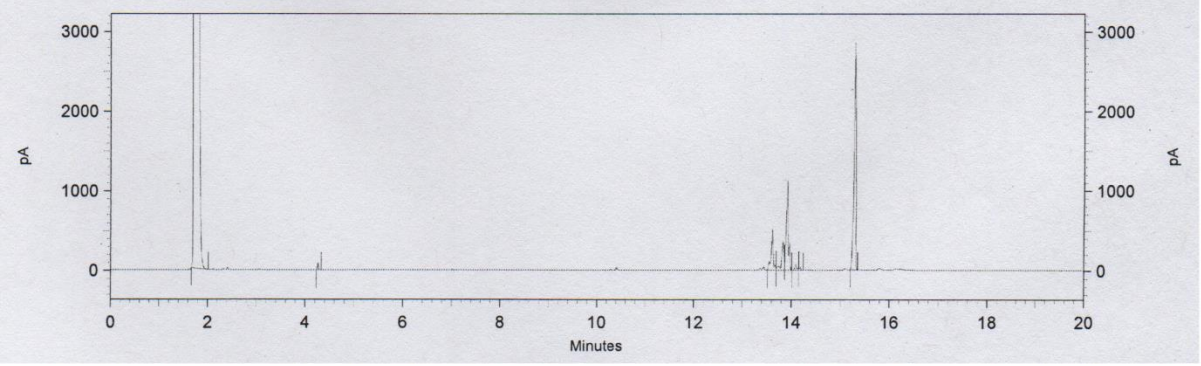


Figure 139 - Phenolic/Squalene (50:50) w/ Sensitizer ZnPh, 1 hour Irradiation

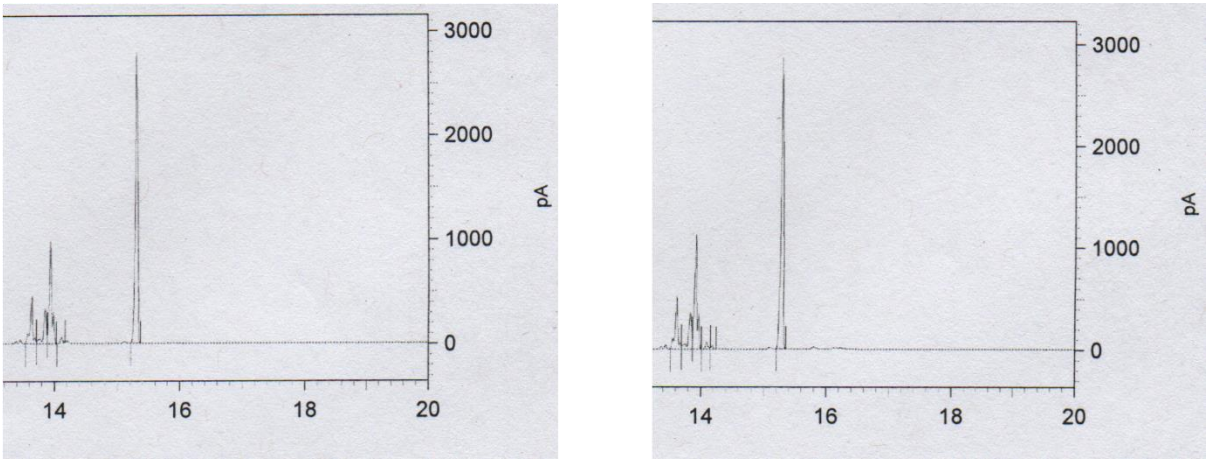


Figure 140 - Phenolic/Squalene (50:50) w/ ZnPh Sensitizer, 1 hour irradiation. Isolated.

10.2.6. Sulfurized Olefin/Squalene

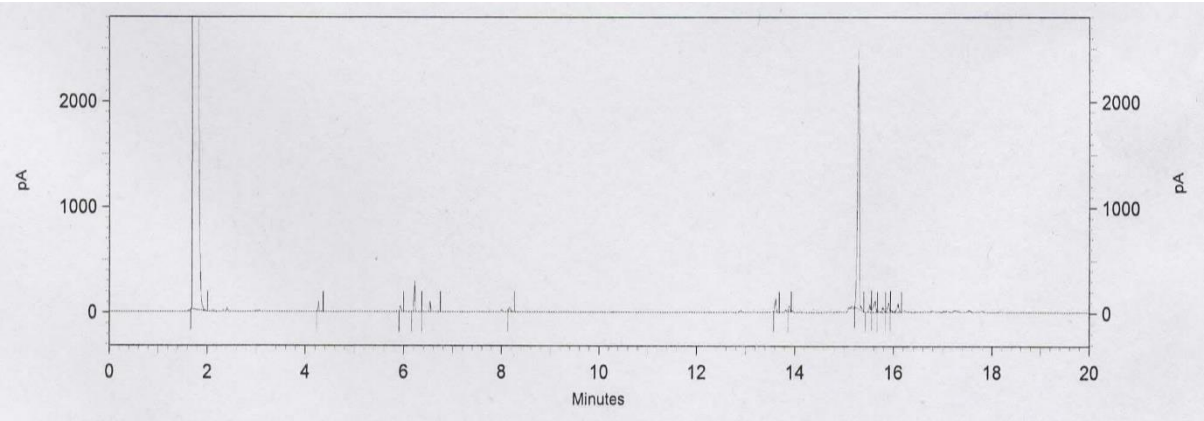


Figure 141 - Squalene/Sulfurized Olefin (50:50)

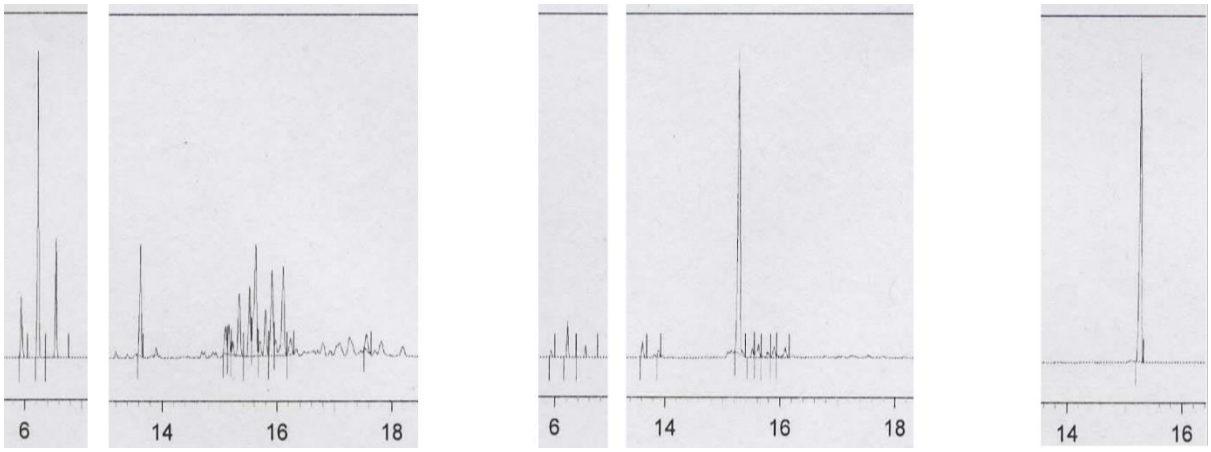


Figure 142 - Comparison of Peaks. Sulfurized Olefin (left), Combined (mid), Squalene (right)

The main issue with the combination of squalene and the sulfurized olefin is that within the individual tests the two antioxidants' peaks for the two occurred around the same time periods, which lead to overlap of peaks. While the squalene was clear and sharp above the rest of the peaks, the sulfurized olefin peaks around 15 to 16 minutes were not picked up as strongly.

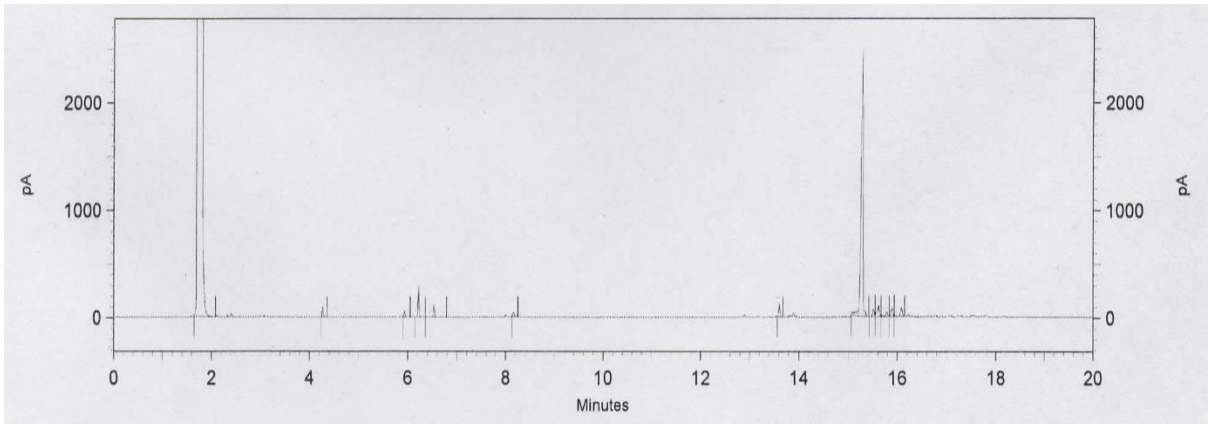


Figure 143 - Squalene/Sulfurized Olefin (50:50) w/o Sensitizer, 1 hour Irradiation

Post a one hour irradiation period there was a slight decrease in the squalene peak, as had been seen previously in the individual tests. There were no significant changes in the sulfurized olefin peaks, although this may have been harder to pick up since the peaks were not very strong. There were no significant changes to these conclusions after the addition of a sensitizer during the irradiation period, suggesting that the squalene changes were most likely due to degradation of the squalene rather than chemical quenching occurring.

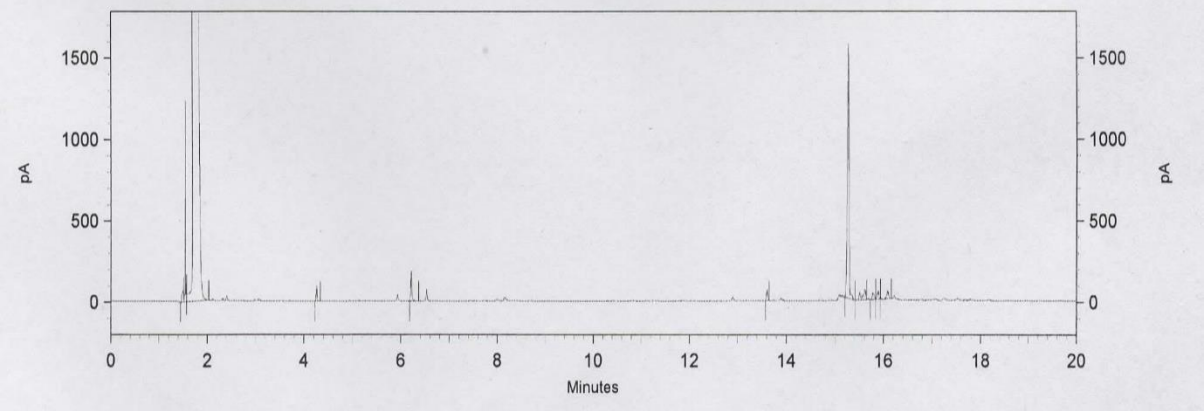


Figure 144 - Squalene/Sulfurized Olefin (50:50) w/ Sensitizer ZnPh, 1 hour Irradiation

10.3. Conclusions

Overall from the data gathered of the individual antioxidants it is clear that gas chromatography certainly has the potential to be a useful technique in the analysis of these antioxidants as singlet oxygen quenchers, specifically in attempting to categorise signs of chemical quenching. That said it is clear that for at least some of the antioxidants, especially the aminic antioxidant, the concentrations used for these types of tests need to be higher to fully register changes.

It is also clear that irradiation times need to be longer to allow for more time for potential chemical quenching to occur to the point where reaction products can be seen within the measurements. This may also require adjustments to be made to the run settings to try and allow for measurement of any new peaks emerging from the noise.

Overall it is difficult to say that this technique would be suitable to obtain at least qualitatively significant information since a significant amount of extra data would need to be obtain before this would be possible with a degree certainty. However, the data gathered so far does suggest that with further data sets over differing irradiation periods it could be possible to observe.

Another factor that should be taken into account in any future testing is the possible degradation of the sensitizers or other products due to the high temperatures applied during the initial injection phase. Therefore, it may be beneficial to attempt further testing using other chromatographic methods, such as high-performance liquid chromatography, which do not require such high temperatures for separation.

11. Conclusions and Future Work

11.1. Conclusions

To conclude this research has shown that all three of the antioxidants provided by Lubrizol have the capacity to quench singlet oxygen, especially the aminic antioxidant. While none of the antioxidants tested showed quenching as strong as that seen by α-tocopherol, the aminic antioxidant did show stronger quenching than that of squalene, the other naturally occurring antioxidant that was tested.

This information suggested that there would be worth in further investigation into the potential use of these naturally occurring antioxidants within lubricant formulation, with squalene being of significant interest due to its structure being favourable for dissolving in hydrophobic organic solvents.

The information gathered also suggests that further research into the potential use of naturally occurring antioxidants is worthwhile, since it has been shown by the results that there are several that are significantly better quenchers than those that were provided by Lubrizol. However, the main issue that was found with α-tocopherol in particular was its thermal instability. Thus, making it an unlikely to be useful within a lubricant formulation since the operating temperatures within the engine block would be too high, causing the antioxidant to break down; which could potentially in turn cause unfavourable side reactions to occur.

11.2. Future Work

11.2.1. Solvent Effects

While this project has looked at a couple of different solvent systems to allow for testing of some of the more hydrophobic antioxidants, the effect of solvents on the quenching rates of these antioxidants or combinations of these antioxidants has not been fully investigated. This would be of interest in the future, since the system these antioxidants work will change over the course of its use. These changes could be in the form of viscosity changes, pH changes as well as the potentially favouring the occurrence of side reactions.

Looking further into the effect of solvents could also be an interesting factor when considering how to adapt the stock oil used in the formulations. By cataloguing any effects from different

solvent systems, including solvent combinations, it may be possible to improve the quality of the base stock and in doing so increase the longevity of the lubricant.

However, the most important factor to test the effect of will be the pH of the solvent system, since apart from viscosity, this is the most probable change that could occur within the solvent system over the lifetime of the lubricant. Changes in the pH are most likely to occur through various reaction that can occur within the solvent from other additives in the mixture.

It is known that the pH of the lubricant oil can drop over time as reactions occur within the engine during combustion that can produce acidic compounds, such as organic acids produced from the combustion of sulphurous compounds. This problem is normally combatted by the addition of highly alkaline compounds, known as over-based detergents, to the lubricant formulation.

However, since these detergents work by reacting with the acidic compounds reducing them to neutralise them, there is only a finite amount that they can reduce. Once these detergents have been used up the acidic compounds can build up in the system unhindered, therefore reducing the pH of the lubricant[59–61].

This problem should not technically arise if the user follows the manufacturer's advice and changes the engine oil regularly. However, this will not always be the case, and as such it would be of interest to see how much this would affect the productivity of the antioxidants.

Overall looking further into solvent effects or generally testing with different solvent systems leads on to the desire to test these antioxidants within actual lubricant oil stocks. This would be an important thing to work towards since this is the solvent that these antioxidants will need to work within in real-world applications. Further to this it would be of interest to study the antioxidants in aged samples, which would give a clearer idea on the timescale in which these antioxidants are effective, be it days, weeks or months, and therefore help in calculating the potential lifetime of the lubricant in a real-world scenario.

However, the method by which this could be achieved would need investigating, especially since aged samples are likely to be very opaque and therefore potentially difficult to impossible to measure using UV/Vis spectroscopy. It may well still be possible to test these types of samples using the luminescence of singlet oxygen if there are no other compounds that will interfere with this.

Another possible testing option would be to consider chromatographic methods to try and split out potential by-products as well as tracking the concentration of an actinometer within the mix. While this could potentially be useful, it also brings with it its own issues, in that with a more complex mixture within the samples there would be a lot more to separate out and try to identify. Therefore, if this were to be investigated as a method it would be best to start out with simpler samples and build up an idea of what to look for in the more complex samples first.

11.2.2. Temperature Studies

While it was not possible to reach similar temperatures to those found within the engine block of a vehicle it was possible to test samples at an increased temperature which was dependant on the solvent being used and the equipment available. This was achieved by flowing heated water from a water bath, set at the desired temperature, around the cell holder as the sample was being irradiated.

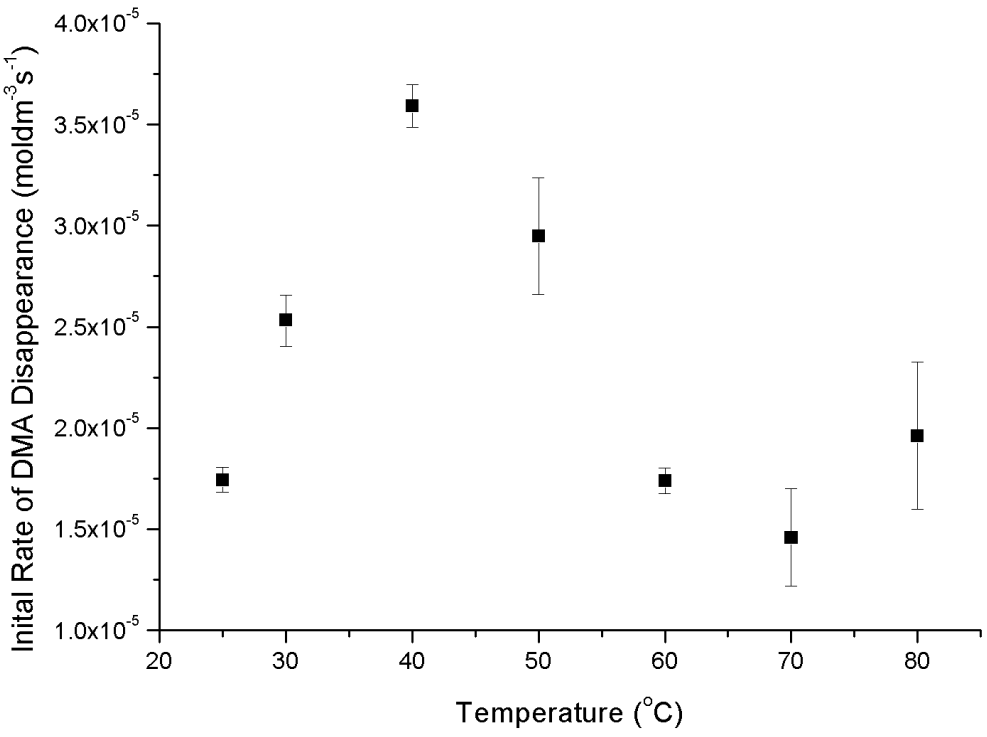


Figure 145 - Rate of DMA Disappearance vs Temperature

There is a slight increase in the initial rate of disappearance of 9,10-dimethylanthracene when increasing the temperature from room temperature, around 25ºC, to 40ºC. However, upon increasing to 50ºC the rate appears to drop back down to around the rate seen for room

temperature, even when factoring in the error. This effect does appear odd since there is an increase in the rate with an increase in temperature initially.

Therefore, it would be of interest to investigate this further with re-runs of the temperatures already covered as well as running the same temperature range with a solution containing only the 9,10-dimethylanthracene to ensure that these effects are due to an increase in the reaction rate with singlet oxygen and not due to an effect of temperature on the stability of the 9,10-dimethylanthracene. It should also be noted that testing at higher temperatures than those already covered will be required to have a fuller example of the conditions found within the engine block. However, to test this would require a different method of heating from that used in these tests, since a water bath would be unable of reaching such temperatures.

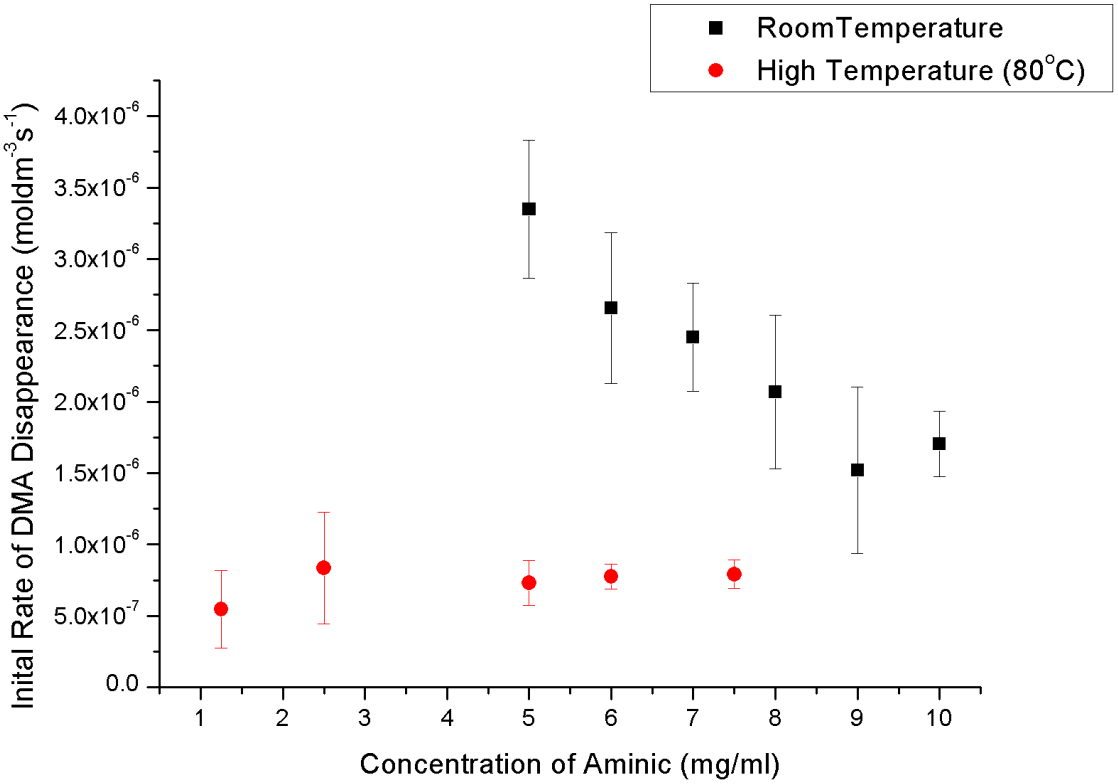


Figure 146 - Rate of DMA Disappearance vs Aminic Concentration at Room Temperature and High Temperature

While at room temperature a clear decreasing trend in the rate of 9,10-dimethylanthracene disappearance can be seen. However, this trend was not seen at the higher temperature where there was no significant change in the rate observed. That said, the overall rates seen at the higher temperature are significantly lower than at room temperature which would suggest that the quenching efficiency of the aminic antioxidant increases at higher temperatures, but that

this efficiency has plateaued, possibly due to being at a point where it is quenching almost, if not as fast as singlet oxygen is being produced.

This is further supported by the fact that the rate of 9,10-dimethylanthracene disappearance with the aminic antioxidant present is over two orders of magnitude lower than the rate seen with 9,10-dimethylanthracene alone at the same temperature.

It would make sense for the aminic antioxidant to be more effective at higher temperatures, since its primary purpose is to work within the conditions found within the engine block, which are even higher than those temperatures tested within this preliminary study.

The results so far also further highlight the need to test the singlet oxygen quenching efficiency of these antioxidants at higher temperatures to see how operating conditions might affect them. This is especially so in the case of the naturally occurring antioxidants α-tocopherol and squalene since their thermostability may suggest that working at higher temperatures will have an adverse effect of their quenching ability.

Another important consideration for future testing would be the solvent used for the samples. 1-Butanol has a boiling point of 116 – 118ºC[99] and while it is fine for use at the temperatures tested so far, it will not be usable at the higher temperatures that would be desired. Hexadecane on the other hand has a boiling point of 287ºC[100] which would allow testing up to temperatures similar to those used in standard tests used for oxidation tests at Lubrizol.

If a higher temperature for testing would be desired then it would be important to find a solvent that would be able to dissolve the sensitizer, acceptor and any antioxidants that want to be tested. Being able to find a suitable testing method for higher temperatures, combined with a suitable solvent that has similar properties to those found in engine oil would be the key for being able to fully test future antioxidants in their singlet oxygen quenching capacity within an engine.

Since the working temperatures for the engine block can reach between 150-300ºC to study at these temperatures would require an effective method of heating the samples which will not impede the ability to take measurements. Suspension within an oil bath may be the most efficient method of heating the samples, however, this would make it more costly to take *in-situ* measurements since it would require a very robust fibre optic probe and might also be more difficult to irradiate the sample efficiently.

Alternatively, it might be possible to utilise a similar set up to that used for the initial temperature study, in that the sample was held within a jacketed sample holder which allowed for the heated water to be circulated around the sample continuously. This however, brings its own issues as the entire set up would have to be confined to a fume hood as well as requiring very robust connectors to limit the risk and potential effects of a leak or spill oh heated oil.

Yet another heating option to consider would be in the use of a heating block or cartridge heater to raise the temperature of the sample holder, similar to the method used previously. This method, if practical, would be the preferable in terms of costs, equipment requirements and associated risks; since it would not involve the use of an oil bath.

11.2.3. Synergies

The main point of interest that was discussed in chapter 8 was the separation of the antioxidant mixtures post testing to look for any signs of chemical reaction between the two antioxidants. This could likely be done through chromatographic separation and could be linked in to further testing using gas chromatography as discussed in chapter 10.

As well as this it could prove useful to test the combinations of antioxidants using the singlet oxygen lifetime measurements as well as the steady-state method to see if this could be a faster, but just as effective, method of testing in the future.

It could also be of interest to see the effect of more combinations of the antioxidants with more antioxidants in each, since a full lubricant additive formulation is not likely to only include the antioxidants tested as there are other factors that need to be accounted for to protect the lubricant, as discussed in chapter 3. However, care would need to be taken in the analysis of such tests as the more components added to the mixture, the more complicated it could become to estimate the effects.

As with the individual tests, it would also be worth testing aged combined samples to look for any potential by-product formation after prolonged exposure to engine conditions.

11.2.4. Cataloguing Antioxidants

Finally, to progress this research further it would be beneficial to create a catalogue or database of the various antioxidants tested, as well as any that might be of interest. This could also extend to cataloguing any variation in quenching with changing of functional groups, giving a better insight into which functional groups may be most beneficial to include in the

development of new compounds. The aim of this would mostly be to aid a research and development team in the creation of new synthetic antioxidants as it can give an idea of which functional groups might be useful to add, and how they might affect the efficiency overall.

This idea could also be used for the synergies to the same end. Cataloguing which types of compounds work together most efficiently and which might hinder each other. This should be of great interest from a business stand point as it could aid in the development and optimisation of future formulations without the need for continuous testing.

11.2.5. Re-runs/Gathering Further Data

There are a couple of the antioxidant results that it would be beneficial to gather more results.

From within the data gathered for the individual quenching constants in hexadecane the data set that it would be most beneficial to re-run or gather further data for would be the naturally occurring antioxidants; α-tocopherol and squalene. With regards to the α-tocopherol data it would be of interest to gather data at the same concentrations as previously used but over a longer period, given that the data showed signs of potential curvature across the testing time. Gathering data over a longer period would help to show if this is in fact the case for this antioxidant, and if so it would be of significant interest to investigate the cause of this.

With the squalene data on the other hand, it would be a definite requirement to re-run the 20mg/ml data set, as this data set showed significant amount of scattering in three out of four to the runs completed. It is possible that this was due to issues with the equipment used however, and re-running the set would allow for clarification on this. Also for the 25 mg/ml data set, since there were some signs of curvature within the data towards the later end of the runs, it would be useful for repeat this concentration over a longer time period as well.

Within the data gathered for the individual quenching constants in 1-butanol, it would be beneficial to re-run all of the data sets at least once for a longer time period than was used within this work, 20 minutes, since a number of the previous runs showed potential signs of curvature within the data towards the 20-minute mark. This was especially true for the data gathered for α-tocopherol, especially when coupled with the similar observations within the hexadecane data.

11.2.6. Alternative Acceptors

Since 9,10-dimethylanthracene is so readily reactive with singlet oxygen it was very useful for testing the efficiency of the antioxidants tested over a fairly short period of time. However, with most of the samples there was eventually curvature seen within the absorption data as the concentration of 9,10-dimethylanthracene became too low to see any significant changes. Therefore, it would be of interest to investigate other potential acceptors for use with the steady-state testing method if testing over a prolonged period of time was needed.

So far, aside from anthracene which was tested alongside 9,10-dimethylanthracene when developing the method, see chapter 6, the only other acceptor that was able to be tested at this time was 1,4-dimethylfuran.

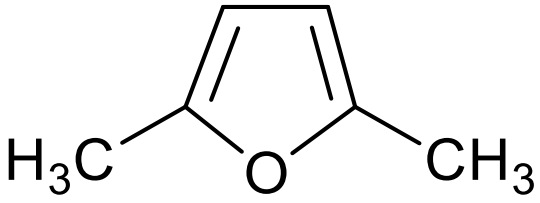


Figure 147 - Chemical Structure of 1,4-dimethylfuran[101]

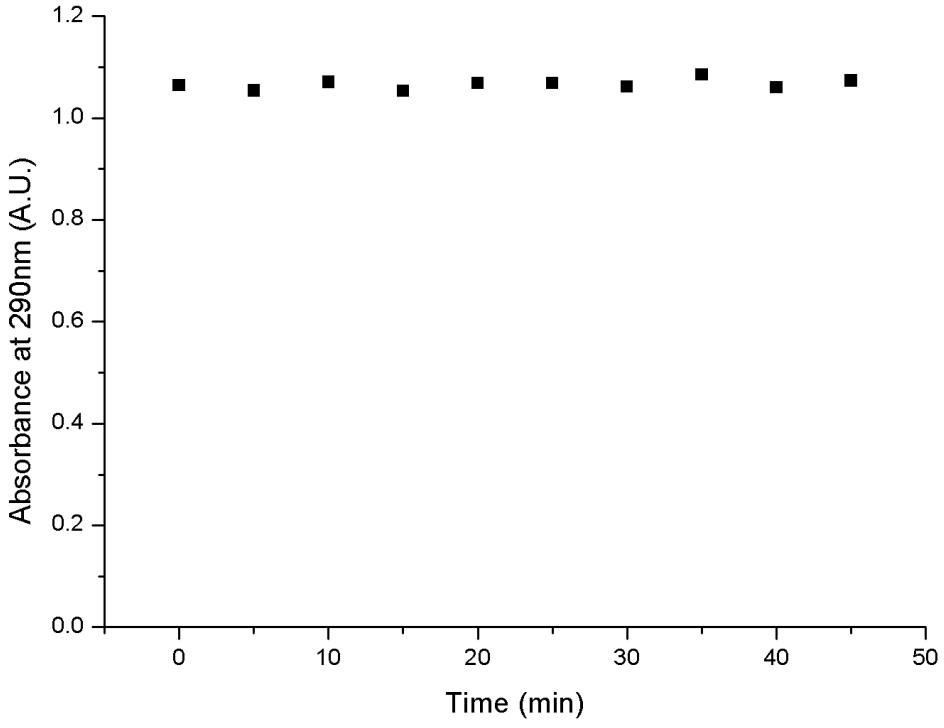


Figure 148 - Absorbance at 290nm vs Time for 1,4-dimethylfuran w/o Sensitizer

When tested with no sensitizer 1,4-dimethylfuran showed no significant change under the LED lamp. This shows 1,4-dimethylfuran to be suitable potential acceptor in the fact that it does not appear to degrade significantly under the lighting conditions, since any notable change in the absorbance at 290nm should only be due to its reaction with singlet oxygen and not degeneration under irradiation.

Upon running with dimethylfuran as the acceptor with a sensitizer present, in this case zinc phthalocyanine to ensure no overlap of peaks and the ability to test in multiple solvent types, the results did not come out as might have been expected. While with 9,10-dimethylanthracene a very clear decrease in the absorbance was seen over time in the presence of singlet oxygen, and opposite trend was seen with dimethylfuran as can be seen below.

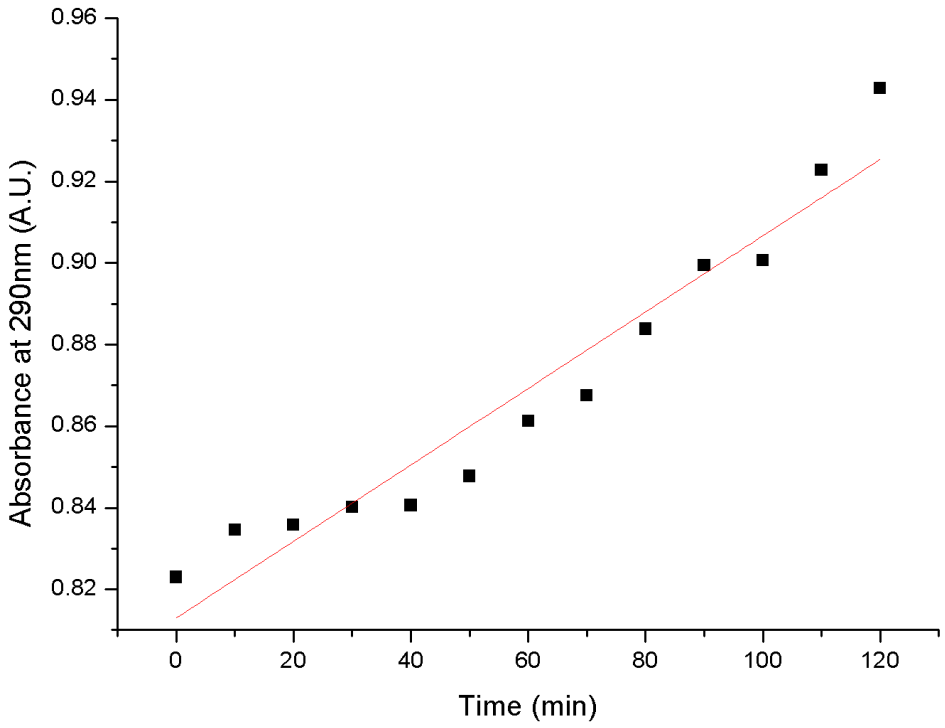


Figure 149 - Absorbance at 290nm vs Time for 1,4-dimethylfuran w/ ZnPh Sensitizer

While this is different it is still possible for this acceptor to be of use since there is still a marked change in the absorbance over time, in the presence of a sensitizer. If the presence of a singlet oxygen quencher significantly effects this change in absorbance, then the acceptor could certainly be used for further investigation.

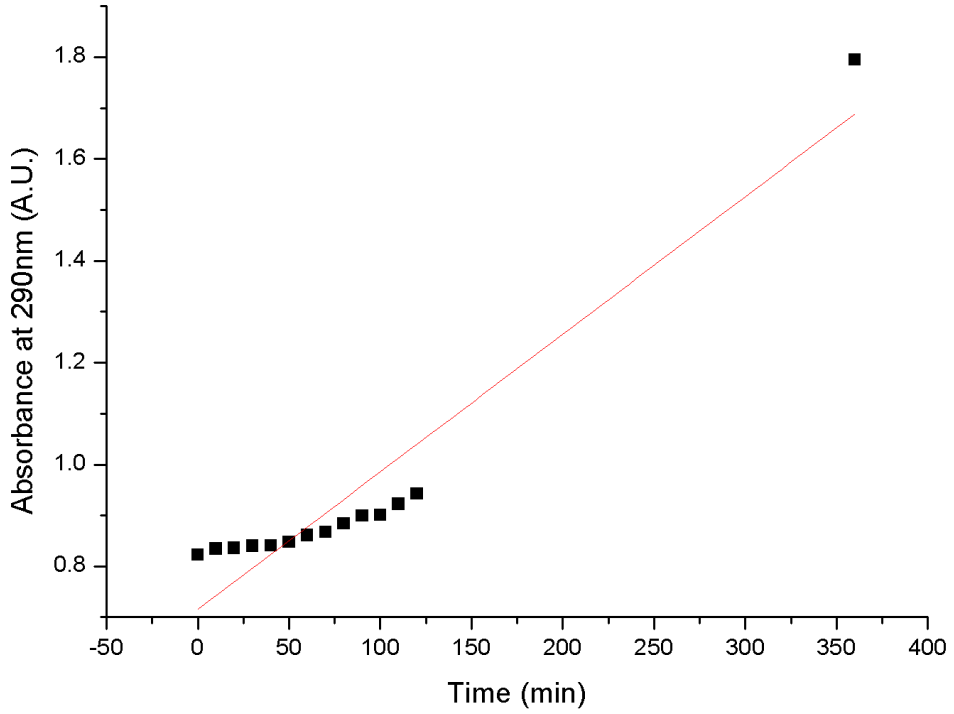


Figure 150 - Absorbance at 290nm vs Time for 1,4-dimethylfuran w/ ZnPh Sensitizer (Longer Duration)

A further test of 1,4-dimethylfuran in the presence of a singlet oxygen sensitizer showed that this trend of increasing absorbance at 290nm continued further over a longer testing duration. Although there were no data points gathered between 120 and 350 minutes the vastly greater absorbance at the later time suggests that there may be a point at which either exponential increases in the absorbance is occurring or that the absorbance has reached a point at which the spectrophotometer can no longer accurately determine the absorbance.

This could prove to be an issue with the use of this compound as an acceptor molecule in the future is prolonged runs are of interest. It also shows that using an acceptor molecule that increases in absorbance over time upon reaction with singlet oxygen could be problematic if the absorbance increases significantly, although this issue may be somewhat negated by the fact that the antioxidants would be quenching at least a portion of the singlet oxygen which is causing this effect.

Overall it would certainly be of use to search for at least a few alternative acceptor molecules that could be used under various testing conditions that may be of interest in the future, and dimethylfuran does show some potential uses in the future.

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