Comparison of hydroxyl radical formation in aqueous solutions at different ultrasound frequencies and powers using the salicylic acid dosimeter.

Louise Milne, Isobel Stewart and David H Bremner
School of Contemporary Sciences, University of Abertay Dundee, 40 Bell Street, Dundee DD1 1HG, Scotland, UK

Abstract
Ultrasonic frequencies of 20 kHz, 382 kHz, 584 kHz, 862 kHz (and 998 kHz) have been compared with regard to energy output and hydroxyl radical formation utilising the salicylic acid dosimeter. The 862 kHz frequency inputs 6 times the number of Watts into water, as measured by calorimetry, with the other frequencies having roughly the same value under very similar conditions. A plausible explanation involving acoustic fountain formation is proposed although enhanced coupling between this frequency and water cannot be discounted. Using the salicylic acid dosimeter and inputting virtually the same Wattages it is established that 862 kHz is around 10% more efficient at generating hydroxyl radicals than the 382 kHz but both of these are far more effective than the other frequencies. Also, it is found that as temperature increases to 42 °C then the total dihydroxybenzoic acid (Total DHBA) produced is virtually identical for 382 kHz and 862 kHz, though 582 kHz is substantially lower, when the power levels are set at approximately 9 Watts for all systems. An equivalent power level of 9 W could not be obtained for the 998 kHz transducer so a direct comparison could not be made in this instance. These results have implications for the optimum frequencies chosen for both Advanced Oxidation Processes (AOPs) and organic synthesis augmented by ultrasound.

Keywords: High frequency ultrasound; salicylate dosimetry; calorimetry; hydroxyl radicals.

1. Introduction

Advanced Oxidative Processes (AOP's) rely on the production of hydroxyl radicals ($HO^{\bullet}$) for the destruction of pollutants. There are a variety of ways in which $HO^{\bullet}$ can be produced in water, usually involving oxidising agents such as O_3 and H_2O_2 along with metal ions or UV/Vis light [1,2]. The most commonly used techniques include the Fenton and related reactions [3,4], ozone and photolysis of ozone [5,6], titanium dioxide/UV light processes [7], hydrogen peroxide/UV light [8] and photo-Fenton reactions [9]. Recently there has been an upsurge in reports on the use of ultrasound to generate hydroxyl radicals especially for wastewater treatment [10] and many studies have been performed in order to maximise the amount of $HO^{\bullet}$ produced by sonication [11-14].

As well as being the second most powerful oxidant, after fluorine, hydroxyl radicals are exceptionally reactive and require specialized techniques for their detection. Electron Paramagnetic Resonance [15], Fricke [16], iodide dosimetry [17] and other chemical dosimeters, where the $HO^{\bullet}$ reacts with organic scavengers, have all been utilised to give relative measurements of hydroxyl radical production. Chemical dosimeters work on the principle that quantification of the products of hydroxyl radical attack gives an indication as to the amount of hydroxyl radicals produced. The terephthalate dosimeter forms 2-hydroxyterephthalate on reaction with $HO^{\bullet}$ and the product can be quantified using fluorescence [18, 19]. However, the most common chemical dosimeter is salicylic acid/salicylate (SA) and this is the technique that was used in this study.

One of the first uses of salicylic acid as a chemical dosimeter to detect hydroxyl radicals was in *in vivo* studies. Hydroxyl radicals were generated by Fenton reactions and the products of hydroxylation of salicylate were separated by HPLC and detected electrochemically [20]. Later work used HPLC-ECD to determine the amount of salicylate hydroxylation as an *in vivo* marker of oxidative stress [21,22] and the mechanisms of hydroxyl radical formation in the hypoxanthine/xanthine oxidase system were estimated using

an HPLC method of dihydroxybenzoic acid quantification [23]. An improved method for determining hydroxyl free radicals *in vivo* using salicylic acid with liquid chromatography and electrochemical detection has also been reported [24] and a similar process was utilised in the assay for free hydroxyl radicals during *in vitro* experiments with thiols [25].

Other than *in vivo* studies little work has been done using the salicylic acid dosimeter. Jen *et al* [26] detected hydroxyl radicals, generated via the Fenton reaction, by measurement of hydroxylated salicylic acids and a similar method was used to study the production of $HO^{\bullet}$ at a lead dioxide electrode [27]. Albarran and Schuler examined the radiolytic oxidation of SA [28], Masten *et al.* used SA as a model compound to investigate hydroxyl radical reactions in the ozonation-membrane filtration hybrid process [29] and SA has been evaluated as a liquid phase scrubbing technique to monitor atmospheric hydroxyl radicals [30]. Hydroxyl radicals can also be formed using hydrodynamic cavitation and Arrojo *et al.* applied salicylic acid dosimetry to evaluate this system as an advanced oxidation process [31]. The operation of a hydrodynamic cavitation reactor was optimised by varying the inlet pressure, shape of the orifice and concentration of SA. Interestingly when hydrodynamic and acoustic cavitation was used simultaneously a 15% increase in hydroxyl radical generation was observed [32]. The intensification of hydroxyl radical production in sonochemical reactors has also been studied. The effect of different operating conditions such as pH, power, additives (haloalkanes, titanium dioxide and iron) and gases (air and oxygen) on the extent of hydroxyl radical production was investigated using SA dosimetry [33]. More recently SA dosimetry has been used to determine the effects of certain parameters of a sonochemical reactor. Using a 2^5 statistical design it was found that only the SA concentration and the reactor geometry were significant factors [34]. This work was extended to an examination of the correlation between hydroxyl radical production and theoretical pressure distribution in a sonochemical reactor [35].

There are a number of requirements when choosing a chemical dosimeter to determine relative $HO^{\bullet}$ production. The reaction rate must be similar to that of hydroxyl radicals (1 x 10^6 to 1 x 10^9 M^{-1} s^{-1}), the oxidation products should be stable and specific to hydroxyl radical attack (not other oxidants such as hydrogen peroxide) and oxidation products must be easily separated and quantifiable with high sensitivity. Salicylic acid meets all these criteria and was utilised in this current work whereby SA and its products were quantified by HPLC and detected with a UV detector. Additionally, SA is relatively non-polar, only slightly soluble and being hydrophobic accumulates at the bubble wall rather than in the bulk solution and is therefore readily available for hydroxyl radical trapping.

Hydroxyl radical attack of salicylic acid can produce 3 main products: 2,3-dihdroxybenzoic acid (2,3-DHBA), 2,5-dihdroxybenzoic acid (2,5-DHBA) and, in some instances, catechol although many other minor products have been identified such as 1,4-dihydroxybenzene, Z,Z-muconic acid, maleic acid, fumaric acid, D,L-malic acid, oxalic acid, malonic acid and acetic acid [36,37]. Depending on the precise reaction conditions many parameters, such as the type of oxidation process, the presence or absence of metals or oxygen, and time of oxidation various quantities of 2,3-DHBA, 2,5-DHBA and catechol can be produced [38], though in the current study only 2,3-DHBA and 2,5-DHBA were detected (Fig 1). Albarran and Schuler [28] note that, in contrast to phenol, the reaction of the electrophilic $HO^{\bullet}$ is favoured at the ortho-position as a result of higher electron density being present at this position due to hydrogen bonding in salicylic acid.

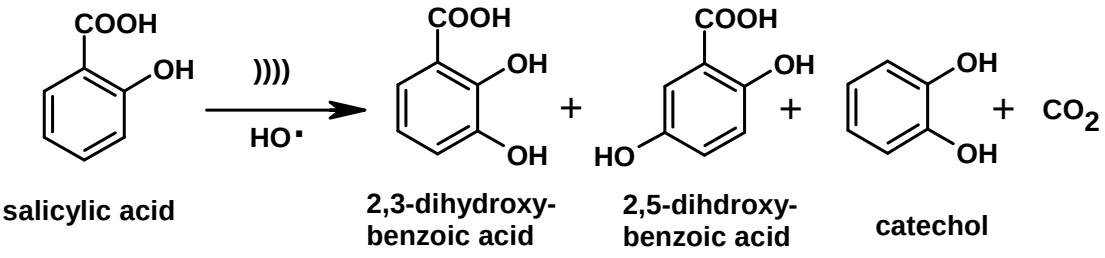

Fig. 1: Main products from the reaction of hydroxyl radicals with salicylic acid.

In any acoustic cavitation event there are millions of cavitation bubbles undergoing transient or stable cavitation [39]. This acoustic cavitation phenomenon is responsible for the production of free radicals [40], however, the experimental conditions e.g. frequency, temperature, intensity, dissolved gases, presence of additives, geometry of reaction vessel and height of reaction liquid all effect hydroxyl radical production, and changes in these parameters can drastically alter acoustic cavitation and alter the amount of hydroxyl radicals produced [34,41-46]. The aim of the current research was to compare hydroxyl radical production at a number of ultrasound frequencies (20 kHz, 382 kHz, 584 kHz, 862 kHz and 998 kHz) and, as far as practicable, to keep the experimental conditions constant.

2. Materials and Methods

A salicylic acid stock solution (500μM; Aldrich) was prepared in deionised water and, for all the experiments; the stock solution (100 mL) was subjected to sonication for 1hr at different frequencies. All solutions, standards and experimental samples were filtered through 0.2μM filter units to remove any particulates prior to use or analysis on the HPLC.

The ultrasound equipment used in these experiments was either a Misonix Ultrasonic Liquid Processor operating at 20 kHz (Fig 2a) or a Meinhardt Ultraschalltechnik high frequency sonicator with a Meinhardt Power Amplifier (Fig 2b). The high frequency sonicator has two transducers: F701 operating at 382 kHz and 998 kHz and the F712 transducer operating at 584 kHz and 862 kHz.

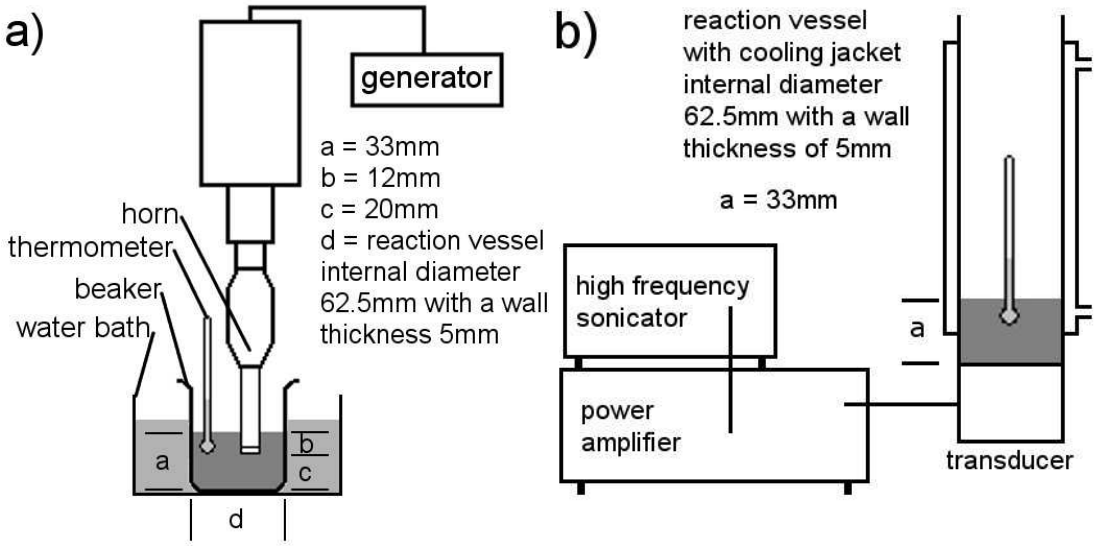

Fig. 2a: The 20 kHz experimental set up: sonicator tip area = 1.2 cm^2, solution volume 100mL.

Fig. 2b: The high frequency set up: transducer area = 22.1 cm^2, solution volume 100mL.

The concentrations of the salicylic acid and its hydroxylated products were quantified by using high performance liquid chromatography (HPLC, Waters 1575 Binary HPLC Pump with 717 plus Auto sampler and 2487 Dual λ Absorbance Detector). The mobile phase was a 60:40 ratio of phosphoric acid (0.02M; pH 2.5) and methanol, with a flow rate of 1 mL min^{-1} , a column temperature of 30 °C and a 20 μL injection volume. The UV detector wavelength was set at 325 nm with a chromatogram run time of 12 min.

Calibration curves for dependency of peak area on concentration were established with standard solutions of salicylic acid as well as its hydroxylated products, 2,3-DHBA (Aldrich) and 2,5-DHBA (Aldrich). Samples were collected every 15 min and filtered before analysis.

2.1 Determination of Power Output of Ultrasound Frequencies by Calorimetry

A thermometer was used to measure the change in temperature of a known volume of deionised water over a specific time and a series of amplitudes were measured for the different frequencies.

For the 20 kHz sonicator a standard volume of water (100 mL) was placed in a 250 mL beaker (internal diameter = 62.5 mm), the probe was positioned 20 mm from the bottom of the beaker and a thermometer was used to allow the temperature to be monitored. The 20 kHz sonication experiments were conducted at 70%, 50%, 30%, 10%, 4% and 1% amplitude and pulsed on for 4s and off for 2s for precisely recorded times.

For the high frequency sonications a standard volume of water (100 mL) was put in the reaction vessel (internal diameter = 62.5 mm). The thermometer was suspended in the liquid to allow the temperature to be monitored. The high frequency sonicator amplitude was varied as required depending on the specific frequency chosen and then sonicated for precisely recorded times.

2.2 Salicylic Acid Dosimetry

2.2.1 Use of 20 kHz Sonication

A standard volume of salicylic acid (500μM; 100 mL) was put into a 250 mL beaker which was then was placed in a 2 L ice bath filled with crushed ice and tap water (400 mL). The 20 kHz sonicator probe was positioned, consistently, 20mm from the bottom in the 250 mL beaker. A thermometer was also positioned in the beaker to allow the temperature to be monitored. The 20 kHz sonicator experiments were all conducted at around 11 W and operated on a pulse mode of 4s on and 2s off until 1 hour of sonication was completed. A sample (2 mL) was removed for HPLC analysis after 0, 15, 30, 45 and 60 minutes of sonication.

2.2.2 High Frequency Sonication

The transducer, rubber gasket and jacketed glass reaction vessel were held together by a Perspex clamp. A standard volume of salicylic acid (500μM; 100 mL) was put in the reaction vessel, a thermometer was suspended in the reaction liquid and cooling was achieved with a flow of cold water through the reactor jacket. The high frequency sonicator amplitude was set at an appropriate amplitude, depending on the specific frequency chosen, and sonicated for 1 hour. A sample (2 mL) was removed for HPLC analysis after 0, 15, 30, 45 and 60 minutes of sonication.

3. Results and Discussion

3.1 Calorimetry

The power output, in Watts, of each frequency was determined by: Watts = Joules s^{-1} and the number of joules was calculated by using $Q = c\ m\ \Delta T$ where Q = number of joules; c = specific heat of water = 4.18 (J g^{-1} °C^{-1}); m = mass of water used (g) and ΔT = change in temp (°C)

All calorimetric measurements were conducted below 33°C, as this was the maximum temperature of the thermometer used, however initial temperatures varied. This variation has no influence on calorimetry results as it has been reported that the temperature rise due to the application of ultrasound is independent of the initial temperature of the liquid between 0 °C and 40 °C [43,47].

The values of the calculated Wattages at the various amplitude settings for the five available frequencies are shown in Table 1. The 20 kHz sonicator shows a reasonable linear relationship between amplitude and wattage though the sonicator was not operated above 70% amplitude in order to prevent damage to the equipment. Of all the available high frequencies, 584 kHz and 862 kHz were the only ones that produced over 9 watts of power, (9.8W and 64W respectively), with the latter being far higher than any of the other as seen graphically in Fig 3. The exact reason why 862 kHz produces at

least 6 times more power is largely unknown and is an area of current investigation. However, one explanation could be the formation of an acoustic fountain, which has been observed at various high frequencies [48]. Visual observations of the operation of the 862 kHz transducer at 9W indicated slight surface deformation and at 64W atomisation was observed making progressive production of an acoustic fountain at increased wattage seem a viable explanation as to why this frequency produced more heat, therefore, giving a higher Wattage than the other high frequencies. The above explanation may account for the fact that all the frequencies are roughly linear when amplitude is plotted against Watts except for 862 kHz (Fig 3).

Table 1: Calculated Wattages at Various Amplitude Settings for the 5 Available Ultrasound Frequencies (n=3)

Frequency (kHz)	**Amplitude Setting**					
	1%	**4%**	**10%**	**30%**	**50%**	**70%**
20 pulsed (4on /2off)	11W	12W	16W	23W	28W	35W
Frequency (kHz)	**Amplitude Setting**					
	35%	**50%**	**65%**	**80%**	**95%**	**100%**
382			3.3W	5.3W	8.0W	7.1W
584			5.7W	8.2W	9.2W	9.8W
862	4W	8.9W	17W	43W	57W	64W
998			1.2W	3.1W	3.9W	4.0W

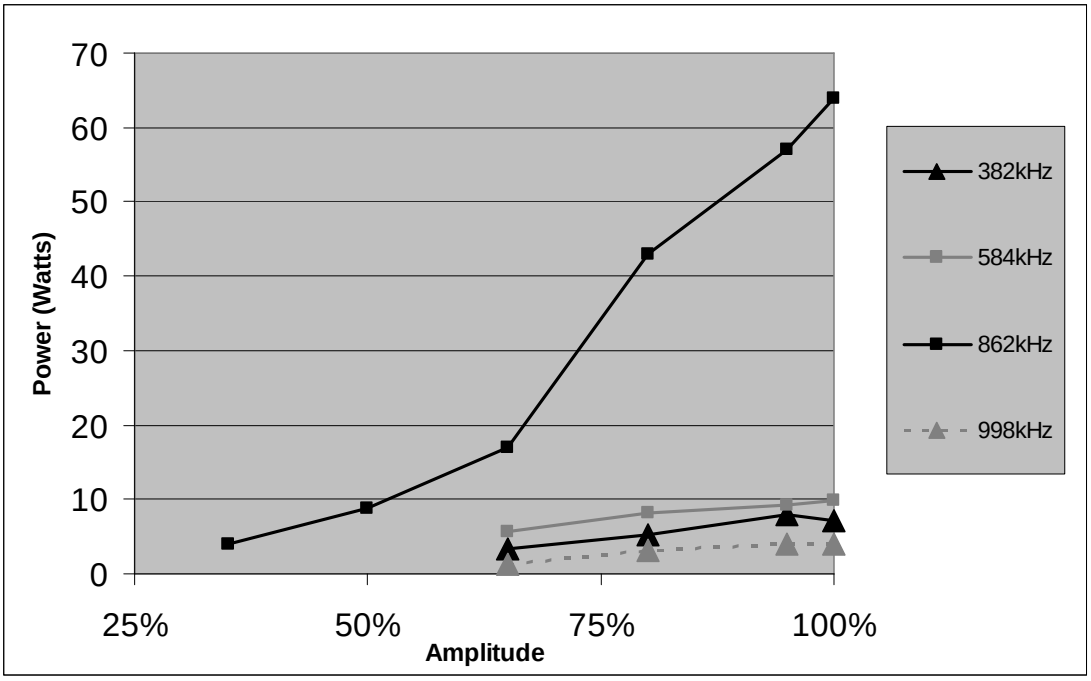

Fig. 3 Graph of Wattage and Amplitude Settings for High Frequency Sonication

3.2 Salicylate Dosimetry

3.2.1 Standard Solutions

For salicylic acid the RSD at all the prepared concentrations was less than 1% indicating the method was precise. This coupled with an average R^2 value of 0.9992, leads to the conclusion that these results were both accurate and precise for determination of salicylic acid concentrations within the range of 50µM to 600µM. Outwith this linear range an estimate can only be made of the concentration from the determined peak area but experimentally the SA concentrations were observed between 350µM to 510µM. Similar results were obtained for 2,3-DHBA (2µM - 20µM; R^2 = 0.9994) and 2,5-DHBA (2µM - 20µM; R^2 = 0.9994) and for all calibration standards RSD = <1%.

3.2.2 Sonication of Salicylic Acid

The application of ultrasound to a solution of salicylic acid (500µM) dissolved in water produced only 2,3-dihydroxybenzoic acid and 2,5-dihydroxybenzoic acid and there were no additional peaks in the HPLC chromatogram to

indicate the production of catechol or any other hydroxyl radical addition products. An estimate of the relative amount of hydroxyl radical production can be made by combining the concentrations of 2,3-DHBA and 2,5-DHBA produced, to give a relative dihydroxybenzoic acid (DHBA) concentration. This DHBA concentration relates to the relative amount of hydroxyl radicals produced but it is not an absolute measure of hydroxyl radical concentration as additional reactions shown in Fig 4 can occur and reduce the number of $HO^{\bullet}$ that escape from the cavitation bubble [49,50].

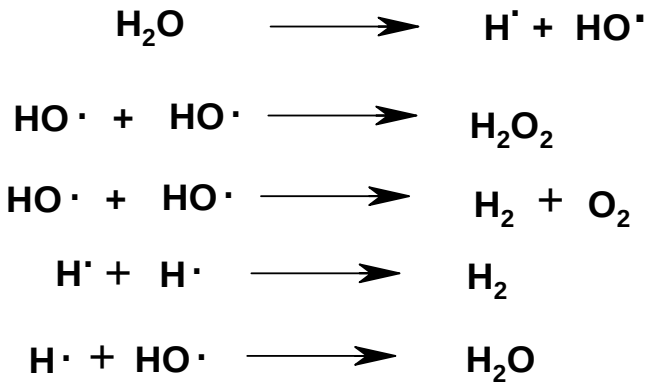

Fig. 4: Fate of hydroxyl radicals

3.2.3. Sonication at 20 kHz

At 11W, the DHBA production is 5.1μM whereas a near 3-fold increase in wattage to 35W results in a 3-fold increase in DHBA production to 14.9μM, therefore, it is assumed there was at least a 3-fold increase in hydroxyl radical production. The intense shear forces produced by 20 kHz ultrasound was evident by erosion of the titanium tip of the 20 kHz probe, resulting in titanium powder appearing in the reaction mixture over time, suggesting that transient cavitation was more prevalent than stable cavitation.

3.2.4 Higher frequency Sonication

With 382 kHz and 5.3W the total DHBA production was 36μM and this increased to around 50μM at 8W. There is no significant difference in total DHBA production at 8W (amplitude 95%) and 7.1W (amplitude 100%). Generally, as intensity increases so does the yield of the reaction, irrespective

of the detection method used, until an optimum is reached beyond which no further increase is observed [51]. It is proposed that for 382 kHz 8W (amplitude 95%) is close to the optimum intensity for this system. With 584 kHz there was little difference in the DHBA production going from 4W (25.4μM) to 9.2W with the highest concentration of 27μM at 8.2W.

When the total concentration of DHBA is plotted against power for 862 kHz it is found to be linear from 3.9W (29.2μM) to 17W and the maximum value at 17W was 81μM. Unlike at 584 kHz the optimum intensity does not seem to have been reached at 862 kHz despite operating at 17W. It was possible to continue to increase the wattage up to the available maximum of 64W, but no experiments were conducted above 17W due to the difficulty in cooling the reaction mixture. Should any future experiments require the wattage to be above 17W, use of a cooling unit would be required so as not to exceed the maximum operating temperature of the transducer (60 °C).

It is proposed that the progression towards creation of an acoustic fountain causes the high power detected at 862 kHz. Although experiments above 17W should significantly increase the production of hydroxyl radicals it is inevitable that an optimum would be reached, though perhaps not within the limits of this equipment. Henglein et al. [52] have shown that increasing the intensity beyond that which produces an acoustic fountain, decreases hydroxyl radical production. Below this threshold level there is deformation of the liquid gas surface and they suggest that this is produced by the surface of the liquid reflecting the ultrasound wave. On formation of an acoustic fountain the surface is disrupted by atomisation, therefore, reflection is reduced and cavitation efficiency is adversely affected resulting in decreased hydroxyl radical production.

For a frequency of 998 KHz it was found that 4W (the maximum output available for this frequency) produced only 3.9 μM of total DHBA.

3.2.5 Input of Similar Wattages

It is very clear that the 862 kHz transducer inputs by far the most energy into the system as reflected in the calorimetric results. However, this startling finding may just be due to the high power available for heating and inducing chemical reactions. Therefore the effect of maintaining the power input constant on the total DHBA production was studied. Fig. 5 shows the differences in DHBA produced after sonication for 60 min with an input of approximately 9W for each transducer. (998 kHz is absent from this figure as this transducer is incapable of generating 9W). A frequency of 862 kHz still produces the most total DHBA (59μM) but 382 kHz is not that much lower (48μM).

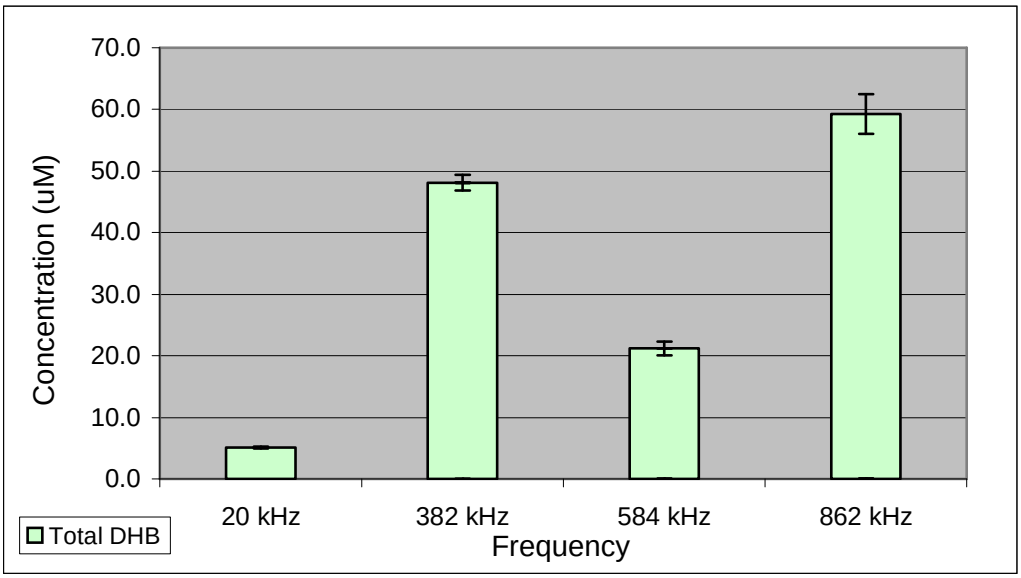

Fig. 5: Graph of production of Total DHBA after 1hr sonication at various frequencies; as shown in table 1 this energy input in each case was approximately 9 W (n=3) and temperature for 20 kHz was 25 ºC ± 1 ºC and the higher frequencies were 38 ºC ± 3 ºC

The calculated RSD values indicate similar levels of consistency between experimental replicates (n=3), with an overall average RSD for these 4 frequencies of 4.2%. The lowest concentration was produced by 20 kHz (5.1μM), however, the 20 kHz experiments were conducted under different operating conditions (pulsed delivery of ultrasound, higher intensity and a probe configuration) compared to the high frequency experiments (continuous delivery of ultrasound and similar intensity at 382 kHz, 584 kHz and 862 kHz).

Although operated under completely different experimental conditions, 20 kHz appears to be the least efficient frequency for production of hydroxyl radicals. This is in agreement with earlier findings [53-55] where 20 kHz was found to be less effective at producing hydroxyl radicals than 500 kHz, 487 kHz and 900 kHz respectively. However, none of these studies utilised the salicylic acid dosimeter.

It is not unexpected that 20 kHz appears to be inefficient in producing hydroxyl radicals, compared to higher frequencies, as large transient cavitation bubbles are produced at low frequency [41]. These bubbles have an estimated lifetime of 300 x 10^{-7}s [56] and violently collapse "entrapping" $HO^{\bullet}$, so that additional reactions are generally favoured [50] over "escape" into the bulk media to react with organic molecules [26]. In comparison, small stable cavitation bubbles are produced at high frequency [50]. The lifetime of bubbles reduces as frequency increases (3 x 10^{-7}s for 514 kHz), however, the number of times cavitation is induced increases at higher frequency [31]. The collapse of these smaller short-lived stable cavitation bubbles is less violent (than transient bubble collapse) allowing the hydroxyl radicals produced to more easily escape into the bulk media to potentially react with organic molecules.

Of the other frequencies studied, (382 kHz, 584 kHz and 862 kHz) a direct comparison can be made as to the levels of total DHBA and hence relative hydroxyl radical production, as operating conditions were generally consistent. Temperature is the only parameter that could not be closely controlled across the three frequencies although there was consistency in temperature with experimental replicates at each frequency (temperature variation is discussed below). Each frequency was applied at 9W and the order of effectiveness was 862 kHz (59.3μM), 382 kHz (48.1μM) and 584 kHz (21.2μM). A previous study showed that as frequency increases, sonoluminescence intensity decreases at the following frequencies: 213 kHz > 355 kHz > 647 kHz > 1056 kHz [45]. It has also been proposed that 200 kHz is the optimum frequency when using iodide dosimetry [51] and H_2O_2 production [57] as methods of

determining levels of produced hydroxyl radicals. In contrast it was found that 358 kHz out performs 205 kHz for destruction of methyl *tert*-butyl ether [58]. Work by Hartmann *et al.* [59] compared drug degradation at 216 kHz, 617 kHz and 850 kHz rating the frequencies as 617 kHz > 216 kHz > 850 kHz. Also the study by Saez *et al.* [60] showed that with *p*-nitrophenol as dosimeter the ratings were 580 kHz > 850 kHz > 380 kHz. Interestingly, these are the only comparative studies using a frequency close to 862 kHz and neither rated 850 kHz as the most effective unlike that found in the present research.

As previously discussed, there are a number of factors that can influence the formation of hydroxyl radicals. A high production of hydroxyl radicals at 382 kHz, using salicylic acid as the dosimeter, is in general agreement with the literature. However, it was not possible, here, to investigate frequencies of ~200 kHz and ~600 kHz which have been reported to produce large amounts of hydroxyl radicals. The most unexpected result was that of 862 kHz having the highest DHBA production of 59.3μM. This is not supported by any prior reports but as previously stated Martinez-Tarifa *et al.* [34] noted that little literature exists for sonochemical studies using salicylic acid as the dosimeter. Although 862 kHz has been used for the degradation of polycyclic aromatic hydrocarbons (PAHs) it was found that 582 kHz out-performed 862 kHz [61].

In the current work the frequency of 862 kHz, and the particular configuration of reaction vessel, may create the optimum conditions for production of hydroxyl radicals. This frequency may also be most favourable for the salicylic acid dosimeter, with regard to cavitation bubble size and release of $HO^{\bullet}$ to the bulk media on cavitation bubble collapse. Although the concentration of salicylic acid remained constant at 500μM for all experiments, the slightly hydrophobic nature of salicylic acid favours the dosimeter residing at the gas-liquid interface. This allows produced hydroxyl radicals easier access to this dosimeter [31], as opposed to one which resides in the bulk media. It may be possible that there is an ideal ratio between the volume of the cavitation bubble at 862 kHz (as frequency determines bubble size), the number of salicylic acid molecules around the bubble in the gas-

liquid interface and the amount of $HO^{\bullet}$ produced on bubble collapse. This would allow efficient oxidation of salicylic acid by a greater number of the hydroxyl radicals produced. In addition, to the solubility of the dosimeter, other factors such as the onset of an acoustic fountain [52] and the possible existence of a unique resonance frequency may also account for the high hydroxyl radical production at 862 kHz.

3.4 Effect of Temperature

It became evident during analysis of results that the temperature of the reaction solution, especially at higher frequencies, plays a role in the amount of total DHBA produced and, therefore, the consistency of experimental replicates (Fig. 5). It has been noted that contrary to the effects seen in traditional chemical reactions, an increase in temperature generally results in a decrease in reaction yield for sonochemical experiments [43,62,63]. Although at 20 kHz it has been shown that lower temperatures favour greater reaction yields [55,64], this was not the case for the high frequencies examined during this project. However, it has been reported that high frequency experiments have an optimum temperature over which reaction yield decreases and this optimum is dependent on frequency, intensity and the detection method [55,64,65].

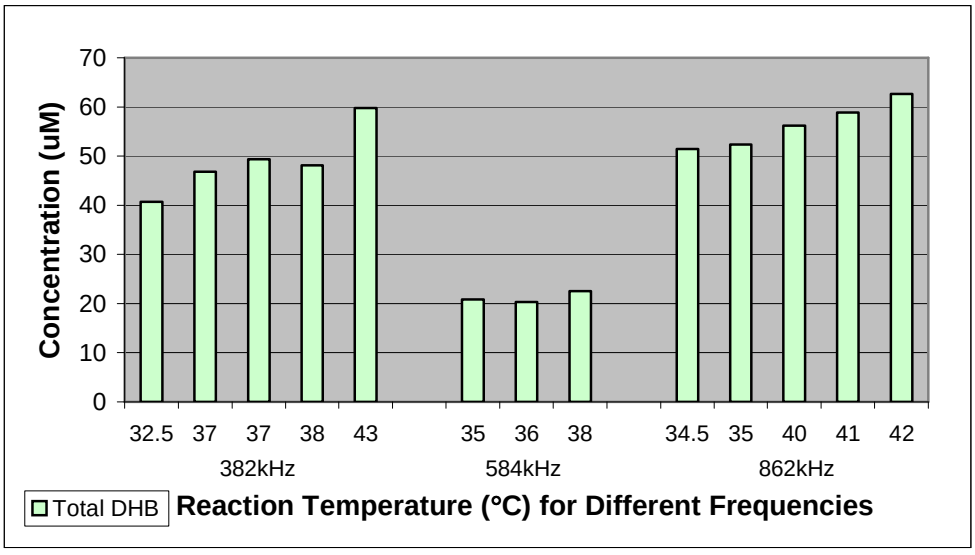

Fig.6: Effects of Reaction Temperature on Total DHBA production at Various High Frequencies after 1hr sonication; approximately 9W

Fig. 6 shows that at 382 kHz, between 32.5 °C and 43 °C, DHBA production and, therefore, hydroxyl radical generation, was more effective as temperature increased. At 300 kHz, Merouani *et al*. [65] found that for 3 detection systems examined over the same temperature range 25 °C to 55 °C, as temperature increased iodine production reduced and Fricke and H_2O_2 production increased. In the present work there was little difference in DHBA production at 584 kHz despite there being a 3 °C temperature difference and this consistency of results may be attributed to the work being carried out within an optimum temperature range. Others have shown that for 500 kHz, between 10 °C and 60 °C, the optimum temperature for production of H_2O_2 (which can be directly attributed to production of hydroxyl radicals) in sonicated water is between 35 °C and 40 °C [64]. Interestingly, at 862 kHz, as the temperature increased from 34.5 °C to 42 °C so did the production of total DHBA (Fig. 6), though at 43 °C, 382 kHz produced virtually same amount of DHBA as the 862 kHz at 42 °C.

4.0 Conclusions

It has been shown that with the high frequency equipment operating at 862 kHz then calorimetry measurements indicate that the amount of energy available is around 6 times that of any of the other frequencies employed. When using a volume of liquid (100 mL), with a concentration of salicylic acid (500μM), operated at an average temperature of 41 °C, 862 kHz is also the optimum frequency for the production of hydroxyl radicals and that the amount produced is greater than that obtained with 382 kHz and 584 kHz, when the power of each is approximately 9W. Further work is on-going in order to determine if 862 kHz is best frequency for hydroxyl radical production when other dosimeters such as terephthalate, p-nitrophenol, Fricke or iodide are used.

References

[1] P.R. Gogate and A.B. Pandit, Adv. Environ. Res., 8 (2004) 501-551.
[2] P.R. Gogate and A.B. Pandit, Adv. Environ. Res., 8 (2004) 553-597

[3] J.J. Pignatello, E. Oliveros, A. Mackay, Crit. Rev. Environ. Sci. Technol*., 36* (2006) 1-84.
[4] D.H. Bremner, A.E. Burgess, F.-B. Li, Appl. Catal. A: General 203 (2000) 111-120.
[5] J. Hoigne, H. Bader, Water Res. 10 (1976) 377-386.
[6] G.R. Peyton, W.H. Glaze, Environ. Sci, Technol. 22 (1988) 761-767.
[7] D. Chatterjee, S. Dasgupta, J. Photochem. Photobiol., (2005) 6 186-205.
[8] F.J. Benitez, A.J. Beltran-Heredia, J.L. Acero Toxicol. Environ. Chem., (1996) 56 199-210.
[9] J.E.F. Moraes, F.H. Quina, C.A.O. Nascimento , D.N. Silva, O. Chiavone-Filho, Environ. Sci. Technol., (2004) 38, 1183-1187.
[10] T.J. Mason, C. Petrier, Ultrasound Processes, in: S. Parsons (Ed.), Advanced Oxidation Processes for Water and Wastewater Treatment, IWA Publishing, London, 2004, pp. 185-208.
[11] K.C. Namkung, A.E. Burgess, D.H. Bremner, Environ. Technol. 26 (2004) 341-352.
[12] R.Chand, N.H. Ince, P.R. Gogate, D.H. Bremner, Sep. Pur. Technol., 67 (2009) 103-109.
[13] R. Kidak, N.H. Ince, Ultrason. Sonochem., 13 (2006) 195-199.
[14] D.H. Bremner, R. Molina, F. Martinez, J.A. Melero, Y. Segura, Appl. Catal. B: Environ. 90 (2009) 380-388.
[15] V. Misik, M. Miyoshi, P. Riesz, J. Phys. Chem., 99 (1995) 3605-3611.
[16] A.K. Jana, S.N. Chatterjee, Ultrason. Sonochem. 2 (1995) 87-91.
[17] D.M. Kirpalani, K.J. McQuinn, Ultrason. Sonochem.. 13 (2006) 1-5. Iodide dosimetry
[18] T.J. Mason, J.P. Lorimer, D.M. Bates, Y.Zhao, Ultrason. Sonochem. 1 (1994) 91-95.
[19] G.J. Price, F.A. Duck, M. Digby, W. Holland, T. Berryman, Ultrason. Sonochem4 (1997) 165-171.
[20] M. Grootveld, B. Halliwell, Biochem. J. (1986) 499-504.
[21] C. Coudray, M. Talla, S. Martin, M. Fatome, A. Fevier, Anal. Biochem. 227 (1995) 101.
[22] C. Coudray, A. Favier, Free Rad. Biol. Med. 29 (2000) 1064-1070.
[23] R.W. Owen, T. Wimonwatwatee, B. Spiegelhalder, H. Bartsch, Eur. J. Cancer Prevention 5 (1996) 233-240.
[24] D.R. McCabe, T.J. Maher, I.N. Acworth, J. Chromatog. B 691 (1997) 23-32.
[25] L. Diez, M-H. A.-A. Livertoux, A.-A. Stark, M. Willman-Rousseau, P. Leroy J. Chromatog. B 763 (2001) 185-193.
[26] J-F Jen, M-F. Leu, T.C. Yang J. Chromatog. A 796 (1998) 283-288.
[27] S. Ai, Q. Wang, H. Li, L. Jin J. Electroanal. Chem. 578 (2005).
[28] G. Albarren, R.H. Schuler, Radiat. Phys. Chem. 67 (2003) 279-285.
[29] B.S. Karnik, S. H. Davies, M.J. Baumann, S.J. Masten Env. Eng. Sci. 24 (2007) 852-860.
[30] R.A. Salmon, C.L. Schiller, G.W. Harris, J. Atmos. Chem. 48 (2004) 81-1004.
[31] S. Arrojo, C. Nerin, Y. Benito Ultrason. Sonochem.. 14 (2007) 343-349.
[32] L.P. Amin, P.R. Gogate, A.E. Burgess, D.H. Bremner Chem. Eng. J. 156 (2010) 165-169.

[33] A.G. Chakinala, P.R. Gogate, A.E. Burgess, D.H. Bremner Ultrason. Sonochem. 14 (2007) 509-514.
[34] A Martinez-Tarifa, S. Arrojo, A.L. Avila-Marin, J.A. Perez-Jiminez, V. Saez, M.L. Ruiz-Lorenzo Chem. Eng. J. 157 (2010) 420-426.
[35] A Martinez-Tarifa, S. Arrojo, O. Louisnard, J. Gonzalez-Garcia, I Tuleda Physics Procedia 3 (2010) 971-979.
[36] C.K. Scheck, F.H. Frimmel Wat. Res. 29 (1995) 2346-2352.
[37] R. Singla, M. Ashokkumar, F. Grieser *Res. Chem. Intermed.* 30 (2004) 723–733.
[38] M. Gruber, G. Wiesner, R. Burger, R. Lindner, J. Chromatog. B 831 (2006) 320-323.
[39] S. de La Rochebrochard, J.F. Blais and E. Naffrechoux Ultrason. Sonochem. 17 (2010) 547-554.
[40] D.H. Bremner, A.E. Burgess, R. Chand Curr. Org. Chem. 15 (2011) 168-177.
[41] J. L. Laborde, A. Hita, J. P. Galtagirone, A. Gérard Ultrason. 38 (2000) 297-300.
[42] P.R. Birkin, T.G. Leighton, D.G. Offin, C.J.B. Vian, In, 20th International Congress on Acoustics, ICA 2010*,* Sydney, AU*,* 23 - 27 Aug 2010.. (2010) pp. 418-423.
[43] L.H. Thompson, L.K. Doraiswamy Ind. Eng. Chem. Res. 38 (1999) 1215-1249.
[44] H.M Santos, C. Lodeiro and J.-L.Capelo-Martinez Ultrasound in Chemistry: Analytical Applications. Edited by José-Luis Capelo-Martínez 2009 WILEY-VCH Weinheim (2009) pp 1-16.
[45] P. Kanthale, M. Ashokkumar, F. Grieser Ultrason. Sonochem. 15 (2008) 143-150.
[46] Y. Asakura, T. Nishida, T. Matsuoko, S. Koda Ultrason. Sonochem.15 (2008) 244-250.
[47] T. Kimura, Takashi Sakamoto, Jean-Marc Leveque, Hajime Sohmiya, Mitsue Fujita, Shigeyoshi Ikeda, Takashi Ando Ultrason. Sonochem.3 (1996) S157-S161.
[48] M. Legay, N. Gondrexon, S. Le Person, P. Boldo, A. Bontemps Int. J. Chem. Eng. 2011 (2011) 1-17.
[49] A. Weissler J. Am. Chem. Soc. 81 (1958) 1077-1081.
[50] Y.G. Adewuyi Ind. Eng. Chem. Res. 40 (2001) 4681-4715.
[51] V.S. Sutkar, P.R. Gogate Chem. Eng. J. 155 (2009) 26-36.
[52] A. Henglein, R. Ulrich, J.Lilie J. Am. Chem. Soc. 111 (1989) 1974-1979.
[53] A. Francony, C. Petrier Ultrason. Sonochem. 3 (1996) S77-S82.
[54] C. Petrier, M-F. Lamy, A. Francony, A. Benahcene, B. David, V. Renaudin, N. Gondrexon J. Phys. Chem. 98 (1994) 10514-10520
[55] M.H. Entezari, P. Kruus Ultrason. Sonochem. 3 (1996) 19-24.
[56] C. Petrier, A. Jeunet, J.-L. Luche, G. Reverdy J. Am. Chem. Soc. 114 (1992) 3148-3150.
[57] C. Petrier, A. Francony Ultrason. Sonochem. 4 (1997) 295-300.
[58] J.W. Kang, H.M. Hung, A. Lin, M.R. Hoffmann, Env. Sci. Technol. 33 (1999) 3199-3205.
[59] J. Hartmann, P. Bartels, U. Mau, M. Witter, W.v. Tümpling, J. Hofmann, E. Nietzschmann Chemosphere 70 (2008) 453-461.

[60] V. Saez, M.D. Escalpez, P. Bonete, D.J. Walton, A. Rehorek, O. Louisnard, J. Gonzalez-Garcia Ultrason. Sonochem. 18 (2011) 104-113.
[61] I.D. Manariotis, H.K. Karapanagioti, C.V. Chrysikopoulos Water Research 45 (2011) 2587-2594.
[62] M.W.A. Kuijpers, M.F. Kemmere, J.T.F. Keurentjes Ultrasonics, 40 (2002) 675-678.
[63] M.H. Entezari, P. Kruus, R. Otson Ultrason. Sonochem. 4 (1997) 49-54.
[64] Y. Jiang, C. Petrier, T.D. Waite Ultrason. Sonochem. 13 (2006) 415-422.
[65] S. Merouani, O. Hamdaoui, F. Saoudi, M. Chiha J. Haz. Mats. 178 (2010) 1007-1014.