Dosimetry in sonochemistry: the use of aqueous terephthalate ion as a fluorescence monitor

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The generation of HO• radicals by acoustic cavitation in water was monitored by their reaction with terephthalic acid (TA) anion to produce fluorescent hydroxyterephthalate ions using a cleaning bath (38 kHz) and a probe system (20, 40 and 60 kHz) as different sources of ultrasound. When using the ultrasonic bath as a source of energy for sonochemical studies, the shape of the reaction vessel is important. In the case of HO• production from water (50 cm³), reaction in a conical flask (100 cm³) produces 2.75 times more radicals than a round-bottomed flask of the same capacity. The fluorescence yield (fluorescence intensity/ultrasound dosage) obtained using the conical flask and ultrasonic bath was similar to that for a probe operating at 40 kHz on the same volume of solution. For a probe system operating at 20, 40 and 60 kHz the greatest sonochemical efficiency was attained at the highest of these frequencies (60 kHz). For the probe system the fluorescence yield is directly proportional to power input and the concentration of TA. The fluorescence yield decreases as the temperature is increased.

Keywords: sonochemistry; dosimetry; fluorescence monitor

With the ever increasing interest in the use of power ultrasound in chemistry – sonochemistry – there is a great need to relate the effects induced by ultrasonic irradiation to the energy used to produce them, one of the most important of which is to establish uniformity for the reporting of sonochemical experiments. Linked to this is the need to be able to reproduce results using different equipment, which requires the determination of the effects which changes in reactor design might induce. With more laboratories exploring the effects of changes in insonation frequencies, there is also a need to characterize the chemical effects of such changes on sonochemistry.

When water is irradiated with ultrasound, hydroxyl and hydrogen radicals are formed as a result of the high energies generated during cavitational collapse (Scheme 1). Evidence for this was presented many years ago by Weissler1, who demonstrated the production of hydroxyl radicals during the sonication of water, and by Anbar and Pecht2, who identified hydrogen radicals. The number of these radicals formed will depend on the cavitation energy of the system. Hence monitoring the radicals produced will provide an estimate of the energy entering a sonicated aqueous medium.

\[
\begin{align*}
H_2O & \rightarrow H^+ + OH^- \\
H^+ + O_2 & \rightarrow HO_2^- \\
HO_2^- + HO_2 & \rightarrow H_2O_2 + O_2 \\
HO_2^- + OH^- & \rightarrow H_2O_2
\end{align*}
\]

Scheme 1  Simplified equations for the production of radicals by sonication

Several methods of monitoring the production of these radicals are available3, the most generally used of which is the estimation of H₂O₂ by iodometry. Three specific methods are in common usage for the estimation of the radical species themselves, namely ESR spin trapping (H• and HO•)4, the oxidation of Fe²⁺ (HO•), known as the Fricke dosimeter5, and the formation of fluorescent hydroxyterephthalate ion (HO•)6. This last method of analysis is relatively easy to perform, is very sensitive and has been used in the determination of the cavitation threshold7,8.

In alkaline aqueous solution, terephthalic acid (TA) produces terephthalate anions which react with hydroxy radicals, HO•, to produce highly fluorescent hydroxyterephthalate ions (HTA) (Scheme 2), the concentration of which can be determined by fluorescence measurements. The reaction provides a very sensitive method of estimating the hydroxyl radicals which enter the bulk liquid having been produced by cavitational collapse.

Using this dosimetry method, it was possible to study the effects of various parameters on the efficiency of HO• radical production. The parameters studied were the intensity, frequency and source of ultrasound together with reagent concentration and reaction temperature. All experiments were performed using either a Kerry
Pulsatrin 55 ultrasonic cleaning bath (38 kHz) or the Undatim Sonoreactor, which has variable frequency and interchangeable acoustic elements to allow studies at 20, 40 and 60 kHz.

Definition of terms used in fluorescence monitoring

Fluorescence intensity ($F$) is the direct reading of fluorescence as recorded on a Perkin-Elmer LS-50 luminescence spectrometer adjusted by subtraction of the small 'zero' reading obtained after the ultrasonic irradiation is switched on and the system attains temperature equilibration. There are no units for fluorescence intensity.

Ultrasound dosage ($D$), in parallel with other radiation dosages, is the ultrasonic power entering the liquid system (W) as recorded by calorimetry multiplied by the time of exposure in seconds. The units of dosage are Ws, i.e. J.

Fluorescence yield is the fluorescence intensity produced per unit ultrasound dosage ($F/D$) and has units of J$^{-1}$.

Results and discussion

Ultrasonic power measurement: calorimetry

The acoustic power entering the system was determined by calorimetry. The temperature ($T$) of the reaction mixture (50 cm$^3$, initial temperature 30 °C) was recorded, using a thermocouple, against time ($t$), at 15 s intervals from the commencement of sonication. The temperature rise ($dT/dt$) at zero times was then obtained using the tangent to the curve at $t = 0$. The ultrasonic power actually entering the system was derived from the equation

$$\text{power} = (dT/dt)C_pM$$

where $C_p$ is the heat capacity of the reactant (J kg$^{-1}$ K$^{-1}$) and $M$ is the mass of reactant used (kg). The power entering each reaction using this method was determined for both the ultrasonic bath (38 kHz) and Undatim Sonoreactor (20, 40 and 60 kHz) operating at different power settings and is summarized in Table 1.

TA as fluorescence monitor using an ultrasonic bath

Effect of sonication time. As can be seen (Table 2) the fluorescence values obtained using the conical flask as a reaction vessel increase with increase in sonication time.

Table 1 Calorimetric determination of power

<table>
<thead>
<tr>
<th>Apparatus Power (W)</th>
<th>Power (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kerry Bath (38 kHz):</td>
<td>17.4</td>
</tr>
<tr>
<td>100 cm$^3$ conical flask</td>
<td>14.7</td>
</tr>
<tr>
<td>Undatim 20 kHz probe:</td>
<td></td>
</tr>
<tr>
<td>Power setting 4</td>
<td>50.4</td>
</tr>
<tr>
<td>5</td>
<td>54.6</td>
</tr>
<tr>
<td>6</td>
<td>61.1</td>
</tr>
<tr>
<td>7</td>
<td>64.8</td>
</tr>
<tr>
<td>Undatim 40 kHz probe:</td>
<td>26.0</td>
</tr>
<tr>
<td>Power setting 4</td>
<td></td>
</tr>
<tr>
<td>Undatim 60 kHz probe:</td>
<td>11.0</td>
</tr>
</tbody>
</table>

$^a$50 cm$^3$ of TA solution ($0.5 \times 10^{-3}$ mol dm$^{-3}$), 30 °C

This is the result of the exposure time or 'dosage' and the influence of dosage is made clear when the fluorescence yield at each time value is deduced. The fluorescence produced ($F$), when divided by the total ultrasonic power entering the reaction vessel, reveals that the fluorescence yield is effectively constant throughout, i.e. if the sonication conditions remain constant fluorescence is directly proportional to exposure time.

Effect of reaction vessel shape. A very significant result follows from observations on the effect of irradiation at 38 kHz using identical conditions except that the reaction was carried out in either an Erlenmeyer or a round-bottomed flask. From Table 2, it is clear that the energies entering the two systems are similar when measured calorimetrically. However, the fluorescence measured after 1 h using the two vessels is substantially different, 28.10 for the conical and 10.20 for the round-bottomed flask, leading to yields of $4.49 \times 10^{-4}$ and $1.93 \times 10^{-4}$ J$^{-1}$, respectively.

A possible explanation for this difference is that the bases for the measurement of energy and fluorescence are different. Energy input is assessed calorimetrically as the total quantity of heat entering the reaction medium including any transmitted as a result of the warming of the glass walls of the vessel. On the other hand, fluorescence is the result of the generation of HO radicals, which can only result from cavitation bubble collapse in the medium. The flat bottom of the conical flask permits more direct transmission of the acoustic energy into the reaction, whereas the curved walls of the round-bottomed vessel deflect much of the acoustic energy. Hence for the same acoustic power in the bath more cavitation will be generated in the former vessel. This emphasizes the importance of the correct choice of vessel geometry when using an ultrasonic bath as sonication source.

TA as fluorescence monitor using an ultrasonic probe

Effect of sonication power. Any increase in ultrasonic power entering the reaction will be associated with an increase in cavitational effect within the system. This, in turn, will produce more HO radicals and consequently greater fluorescence as more HTA is produced. Evidence of this is provided by the fluorescence yield obtained after 1 h of sonication using an Undatim Sonoreactor (20 kHz) at four different powers (Table 3). Irrespective of the initial concentration of TA, the fluorescence yield at all four...
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Table 3 Effects of ultrasonic intensity and TA concentration on the TA dosimeter using a probe (20 kHz)\(^a\)\(^b\)

<table>
<thead>
<tr>
<th>Conc. (^c)</th>
<th>Power setting</th>
<th>(4)</th>
<th>(5)</th>
<th>(6)</th>
<th>(7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>30.00</td>
<td>1.65</td>
<td>30.64</td>
<td>1.56</td>
<td>36.89</td>
</tr>
<tr>
<td>1.0</td>
<td>59.15</td>
<td>3.26</td>
<td>59.33</td>
<td>3.02</td>
<td>67.68</td>
</tr>
<tr>
<td>1.5</td>
<td>84.45</td>
<td>4.65</td>
<td>85.98</td>
<td>4.37</td>
<td>94.51</td>
</tr>
<tr>
<td>2.0</td>
<td>106.30</td>
<td>5.86</td>
<td>113.11</td>
<td>5.75</td>
<td>125.24</td>
</tr>
</tbody>
</table>

\(^a\)50 cm\(^3\); sonication time 60 min; \(T = 30^\circ C\)

\(^b\)Fluorescence yield \(\times 10^{-4}\) J\(^{-1}\); mean of two runs, reproducibility \(\pm 2\%\)

\(^c\)Concentration of TA \(\times 10^{-3}\) mol dm\(^{-3}\)

Table 4 Effects of ultrasonic frequency and TA concentration on the TA dosimeter using a probe\(^d\)

<table>
<thead>
<tr>
<th>Concentration ((10^{-3}) mol dm(^{-3}))</th>
<th>Fluorescence(^d)</th>
<th>20 kHz</th>
<th>40 kHz</th>
<th>60 kHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>30.00</td>
<td>1.65</td>
<td>40.24</td>
<td>4.30</td>
</tr>
<tr>
<td>1.0</td>
<td>59.15</td>
<td>3.26</td>
<td>68.29</td>
<td>7.30</td>
</tr>
<tr>
<td>1.5</td>
<td>84.45</td>
<td>4.65</td>
<td>102.69</td>
<td>10.97</td>
</tr>
<tr>
<td>2.0</td>
<td>106.30</td>
<td>5.86</td>
<td>131.71</td>
<td>14.07</td>
</tr>
</tbody>
</table>

\(^d\)50 cm\(^3\); sonication time 60 min; power setting 4 (20 kHz = 50.4 W, 40 kHz = 26 W and 60 kHz = 11 W); \(T = 30^\circ C\)

\(^e\)Fluorescence yield \(\times 10^{-4}\) J\(^{-1}\); mean of two runs, reproducibility \(\pm 2\%\)

settings remains effectively the same, i.e. the yield of HO\(^-\) radicals is directly proportional to power input.

**Effect of TA concentration.** The fluorescence intensity for a given ultrasonic dosage is directly proportional to the concentration of TA in solution (Table 3). This can be rationalized in terms of the greater probability of reaction between the HO\(^-\) radicals produced and the trapping agent (TA) available in the bulk solution, rather than reaction by collision with other species. The remarkable uniformity in fluorescence yield at each concentration but at different powers again suggests that fluorescence is an excellent technique for ultrasonic dosimetry.

**Effect of ultrasonic frequency.** Historically there have been two underlying misconceptions in sonochemistry. The first suggests that sonochemical reactions are unaffected by changes in irradiation frequency. This arises from the idea that once the cavitation threshold is exceeded, the ensuing cavitation collapse will provide the same effects whatever the frequency. The second is that sonochemistry is always performed at frequencies within the power ultrasound range, normally defined as 20-100 kHz. However, there is a considerable amount of information on sonochemistry which uses higher frequencies, i.e. in the ultrasonic range (around 1 MHz), yet still involves cavitation\(^f\). Some interesting frequency effects occur even within the kHz range. Consider, for example, the generation of H\(_2\)O\(_2\) during the sonolysis of water. The hydrogen peroxide is produced as a result of various radical recombination reactions (Scheme 1) and can be estimated by iodometry. In an important paper on this topic, Petrier et al.\(^{10}\) compared the effectiveness of 20 and 514 kHz irradiation in the oxidation of aqueous KI to iodine at the same input power. The rate of production of iodine in oxygen-saturated KI (0.01 mol dm\(^{-3}\)) was about six times greater at the higher frequency. This result was ascribed to the fate of the HO\(^-\) radical which can be destroyed by reactions in the bubble or can migrate into the bulk and produce peroxide. At the higher frequency a shorter bubble lifetime allows more of the HO\(^-\) to escape from the bubble. We have investigated this frequency effect over a much narrower frequency range using the HTA fluorescence monitor.

The results of fluorescence intensity measurements at different sonication times for 50 cm\(^3\) samples at three different frequencies are shown in Table 4. It can be seen that after 60 min of irradiation the 40 kHz probe gives the best result in terms of fluorescence intensity at all of the concentrations employed. However, this does not take into account the ultrasonic power used. When the power is taken into account the fluorescence yields are uniformly greater at the highest frequency (60 kHz); in fact, the ratio of fluorescence yields at 20, 40 and 60 kHz (Table 4) is approximately 1:2:4 throughout the study. This indicates that, within the narrow range of frequencies chosen in this part of the study, 60 kHz is the best frequency for the formation of HO\(^-\) radicals. This finding is in accord with that of Petrier et al.\(^{10}\) that the higher frequency of 514 kHz was more efficient than 20 kHz for HO\(^-\) radical production. Naturally, such generalizations must have a limit in that at sufficiently high frequencies cavitation will not be possible and so no radicals will be generated.

**Effect of temperature.** Table 5 shows the variation of fluorescence intensity with concentration of TA for samples sonicated at 30 and 90 \(^\circ\)C for 60 min. The results show clearly that with sonication at the higher temperature there is a decrease in the fluorescence emission. In fact, the power entering the system at 90 \(^\circ\)C (26 W) is about 50\% of that entering at 30 \(^\circ\)C (50.4 W). The effect of bulk temperature on radical production can be ascribed to a
Table 5 Effect of temperature on the fluorescence intensity and yield of HTA at different concentrations

<table>
<thead>
<tr>
<th>Concentration (10⁻³ mol dm⁻³)</th>
<th>Fluorescence⁶</th>
<th>Yield</th>
<th>Fluorescence⁶</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30°C</td>
<td>90°C</td>
<td>30°C</td>
<td>90°C</td>
</tr>
<tr>
<td>0.5</td>
<td>30.00</td>
<td>1.65</td>
<td>12.60</td>
<td>1.35</td>
</tr>
<tr>
<td>1.0</td>
<td>59.15</td>
<td>3.26</td>
<td>24.30</td>
<td>2.60</td>
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<tr>
<td>1.5</td>
<td>54.45</td>
<td>4.65</td>
<td>36.20</td>
<td>3.87</td>
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<tr>
<td>2.0</td>
<td>106.33</td>
<td>5.86</td>
<td>45.20</td>
<td>4.83</td>
</tr>
</tbody>
</table>

⁶50 cm³; sonication time 60 min; 20 kHz, power setting 4 (50.4 W at T = 90°C).

As the concentration of TA increases, the fluorescence intensity increases, but the temperature effect still remains.

Comparison of the effects of using a bath and a probe system in fluorescence monitoring

An interesting comparison can be made between the efficiency of an ultrasonic bath and a probe system for radical generation. From Table 2 it can be seen that after 60 min of irradiation using a bath (38 kHz) a 0.5 x 10⁻³ mol dm⁻³ solution of TA gives a fluorescence yield of 28.10 or 10.20 depending on whether a conical or round-bottomed reaction vessel was used. Using a 40 kHz probe system the yield obtained with the same solution was 40.24 (Table 4). This appears to suggest that the probe is more efficient than a bath for the generation of HO radicals. However, when the fluorescence yield is calculated for these systems it becomes clear that the yield for the conical reactor system (4.49 x 10⁻¹ J⁻¹) and that for the probe (4.30 x 10⁻¹ J⁻¹) are remarkably similar, whereas the round-bottomed reactor gives a substantially lower yield (1.93 x 10⁻¹ J⁻¹). This result appears to indicate that for this particular dosimetry system the conical flask is not only more efficient than the round-bottomed flask for HO generation in an ultrasonic bath, but also that the efficiency of the reaction in a conical flask is similar to that obtained with a probe operating at the same frequency.

Experimental

Preparation of 2-hydroxyterephthalic acid (HTA)

2-Bromoterephthalic acid (25 g; 0.102 mol) and sodium hydroxide (8.2 g; 0.204 mol) were dissolved in 470 cm³ of water. After the addition of sodium acetate (18.4 g; 0.224 mol), copper powder (0.13 g) and a few drops of phenolphthalein, the aqueous mixture was stirred and heated at reflux for 10 h. Aqueous potassium hydroxide (8.2 g; 0.182 g (2.2 x 10⁻³ mol) and sodium hydroxide (0.981 g; 0.294 g (2.2 x 10⁻³ mol) were added to the reaction mixture. After cooling, the mixture was filtered, and the filtrate was acidified with HCl (2 mol dm⁻³). The white crystals were collected by filtration and dried in a vacuum oven. The yield of HTA was 17.92 g (96.50%); m.p. 320-325 °C (lit. m.p. 320-322 °C).

A stock solution of the standard 2-hydroxyterephthalic acid (HTA) was prepared, with the composition HTA 0.182 g (1.0 x 10⁻³ mol), NaOH 0.100 g (2.5 x 10⁻³ mol) and phosphate buffer (pH 7.4), made up from KH₂PO₄ 0.294 g (2.2 x 10⁻³ mol) and Na₂HPO₄ 0.491 g (3.5 x 10⁻³ mol). Volumes of solution of 500 cm³ were made up with water. The concentration of the solution with respect to HTA was 2.0 x 10⁻⁵ mol dm⁻³. The stock solution was diluted initially to a concentration of 2.0 x 10⁻⁵ mol dm⁻³ (1 cm³ to 100 cm³) and then using this solution, further dilutions of known concentration were made.

The fluorescence of each solution was measured using a Perkin-Elmer LS-50 luminescence spectrometer with an excitation wavelength of 315 nm and an analyzing wavelength of 425 nm. A graph of fluorescence intensity against HTA concentration was plotted and gave a straight line of positive slope for concentrations from 0.2 x 10⁻⁵ to 2 x 10⁻⁵ mol dm⁻³. Hence it can be assumed that the fluorescence intensity generated by sonications of samples is proportional to the concentration of the HTA in the samples and is thus a measure of the quantity of HO radicals liberated by cavitation collapse.

Sonolysis of aqueous terephthalic acid solutions

A stock solution of terephthalic acid (TA) was prepared, with the following composition: TA 0.332 g (2.0 x 10⁻³ mol), NaOH 0.200 g (5.0 x 10⁻³ mol) and phosphate buffer (pH 7.4), made up from KH₂PO₄ 0.589 g (4.4 x 10⁻³ mol) and Na₂HPO₄ 0.981 g (7.0 x 10⁻² mol). This was them made up to 1000 cm³ with water, giving a concentration with respect to TA of 2.0 x 10⁻⁵ mol dm⁻³. Dilutions of this stock TA solution provided four different initial concentrations, 0.5 x 10⁻³, 1.0 x 10⁻³, 1.5 x 10⁻³ and 2.0 x 10⁻³ mol dm⁻³.

Using a bath

Aqueous TA (50 cm³) was placed in a 100 cm³ conical or round-bottomed flask and sonicated using a Kerry Ultrasonics Pulsatron 55 bath (Kerry Ultrasonics, Hitchin, Herts, UK). The sample was placed in the same central position each time and at the same depth in the bath water, by means of a template. Constant temperature was maintained by adding ice periodically to the bath water. The ice did not significantly alter the energy entering the reaction systems because the ice floated on the surface and the reaction vessels were immersed well below the surface of the bath liquid.

Using a probe system

A dimple cell was used as the reactor in these experiments. This is a glass tube sealed at the base from which an indentation (dimple) protrudes into the cell. This indentation provides efficient mixing of liquid contents as the streaming produced by probe sonication impinges upon it (a fuller description of the dimple cell and other reactors can be found elsewhere). A 50 cm³ volume of aqueous TA was placed in the cell and sonicated, using an Undatim Sonoreactor (Undatim Ultrasonics, Louvain-la-Neuve, Belgium), which has interchangeable acoustic elements enabling it to be used at a number of different frequencies. The temperature within the reaction vessel...
was maintained using a constant-temperature bath set below the reaction temperature, thus allowing for the heating due to sonication.

**Analysis**

For each kinetic run aliquots of the sonicated solution (2.0 cm$^3$) were withdrawn and diluted according to their initial concentrations such that the effective initial concentration of TA in the analysed sample was 0.5 \times 10^{-3} \text{ mol dm}^{-3}. Fluorescence measurements were carried out as soon as possible after sonication. The samples were stored in the dark as recommended, although, in our hands, no significant change in hydroxyterephthalate concentration was observed in normal light over the period of a typical reaction at room temperature. The fluorescence intensity was determined using the LS-50 spectrometer as above. On removal of an aliquot for fluorometric analysis, the overall reaction volume for sonication is reduced. In order to eliminate this problem, 2 cm$^3$ of TA solution of the same concentration and at the same temperature as that used for the kinetic run were added after each withdrawal of an aliquot.

**Conclusions**

Terephthalic acid (TA) dosimetry is a viable method for monitoring the cavitational effects of power ultrasound in aqueous media.

The use of fluorescence yield (fluorescence intensity/ultrasound dosage) provides a measure of the efficiency of production of HO$^-$ radicals via sonication. It should be remembered, however, that this method employs a chemical dosimeter and as such it may not be the ideal dosimeter for estimating sonochemical reactions which rely on only the mechanical effects of ultrasound. When using the TA dosimetry method for sonication at 20, 40 and 60 kHz, the greatest sonochemical efficiency was attained at the highest of these frequencies (60 kHz). When using an ultrasonic bath as a source of energy for sonochemical studies, the shape of the reaction vessel is important. In the case of HO$^-$ production from water (50 cm$^3$) a conical flask (100 cm$^3$) is more efficient than a round-bottomed flask of the same capacity. The fluorescence yield obtained from an ultrasonic bath at 38 kHz using the conical flask was similar to that of a probe operating at 40 kHz on the same volume of solution.

**Acknowledgements**

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**References**

3. For general descriptions of methodologies for dosimetry, see Mason, J.J. Practical Sonochemistry Ellis Horwood, Chichester, UK (1991)
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