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A 1 kHz resolution frequency study of a variety of sonochemical processes

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A variety of reactions, which are known to be enhanced or driven by sonochemical effects, have been studied and their absolute rate measured as a function of the ultrasonic frequency employed within a cylindrical reactor. The rate is shown to be highly dependent on the ultrasonic frequency employed in the range of 20 kHz to 160 kHz. The frequency dependence of the system is the net result of the frequency dependencies of the transducer, the reverberant sound field, the cavitation dynamics and the chemistry. Rate variation of the reactions studied is correlated to light emission (sonoluminescence) as a function of the acoustic driving frequency with a resolution down to 1 kHz. The results are discussed with reference to the acoustic characteristics (particularly the modal nature) of the cell employed. The results are compared to the spatial peak acoustic pressure amplitude within the cell and broadband audio emission. Chemical activity could be predicted by sonoluminescence activity, which correlated with the more spatially complex sound field produced at higher frequencies. The most important finding is that characterisation of the sound field is vital in sonochemical experiments: a $<3\%$ change in the driving frequency was found to change the chemical activity by 3 orders of magnitude, because of the tuning effect of the modal sound field.

Introduction

Ultrasound can accelerate a wide variety of homogeneous and heterogeneous reactions through the production of cavitation.[1–4] It is postulated, from a variety of experimental evidence, that the observed homogeneous chemical effects are caused by the high localised pressures and temperatures[5] produced within the interior of a cavitation bubble.

The phenomena of multi or single bubble sonoluminescence [MBSL or SBSL] are also associated with cavitation bubble collapse.[6,7] Considering the similarities between the conditions required for both MBSL and sonochemical effects, one might expect that measurement of light output of a sonochemical reactor should give a good indication of chemical activity.[8,9] This has been highlighted in a number of studies.[9,10] However, in some reports it has been shown that luminescence is not proportional to sonochemical reaction rates.[11] This manuscript outlines a study of a number of sonochemical reactions and suggests that an understanding of the sound field is beneficial in the interpretation of sonochemical data.

Many sonochemical reactions involve the generation of radical species[12–15] produced by the extreme conditions generated in the collapse of a cavitation bubble. In many instances it is not possible to detect the presence of these radicals directly. However, evidence for radical species is gathered by the employment of radical trap reagents and ESR experiments.[12] It is also possible to redox trap highly oxidising/reducing species (which are both associated with the primary generation of radicals) with a number of well known reactions. Examples of such systems that operate in this manner include the Weissler[1] and Fricke[14,16,17] reactions. There are many studies on the influence of ultrasound on the rate of a chemical reaction. However, in general the frequency of sound employed is usually kept to a few fixed values often separated by 100's kHz.[10,18–20]

In this paper we also compare the variation of light emission, acoustic pressure, broadband airborne audible noise and reaction rates as a function of the driving frequency employed within a simple sonochemical reactor.[21] The results demonstrate the importance of precise and accurate control of experimental conditions and equipment design. In addition a 1 kHz frequency resolution study of luminescence, reaction rates and acoustic measurements is reported for the first time.

Experimental

Chemicals

Sodium chloride (BDH, 99.9%), hydrochloric acid (BDH 35.4%), sulfuric acid (BDH 98%), meldola blue (BDH), potassium iodide (Hogg, 99%), iron(II) sulfate heptahydrate (Aldrich 99%), copper (II) sulfate 5-hydrate (BDH, 99%) potassium sulfate (BDH, 99.5%), sodium sulfate (BDH, 99%), hexaamine ruthenium (III) chloride, $[Ru(NH_3)_6]Cl_3$ (Strem Chemicals, 99%), luminol (3-aminophthalhydrazide, Aldrich 97%), sodium carbonate (BDH, 99.5%), potassium dihydrogen orthophosphate (BDH, 98%), were used as received. Aqueous solutions were prepared with water purified from either an USF Elga Elect 5® or Vivendi Purelab Option E10 water purification system. This system produced high quality water with a resistivity $\sim$15 MΩ cm and a TOC $<$30 ppb†.

Apparatus and procedure

Experiments were carried out within a 25 °C temperature controlled cylindrical jacketed glass cell containing 100 cm^3 of aerobic (air equilibrated) solution. The internal diameter

† Data supplied by manufacturer.

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of the cell (an important parameter for predicting the acoustic modes[21]) was 5.8 cm. The cell was attached to a sandwich transducer (Morgan Electro Ceramics Ltd) with epoxy resin (Struers, Epofix). A water-jacketed system was employed to maintain temperature control. This cell had a sandwich transducer with a resonance frequency *ca.* 27 kHz, transducer properties (air) Q factor 900 ± 200, resonant impedance $15 \pm 5\ \Omega$, effective coupling coefficient 0.37 ± 0.02 and shunt capacitance 3.7 nF.[22] A programmable function generator (Thurlby Thandar Instruments, TG1010) was used to generate a signal at the required frequency. The signal was amplified (Brüel & Kjaer 2713 Power amplifier) before driving the transducer. The post amplification voltage (zero to peak) across the transducer was (maintained at 100 V in all experiments) measured using a Tektronix TDS 224 oscilloscope. The emission of light was measured in a dark room using an EG&G Photon Counting (module SPCM-200-PQ). The photon counter was positioned vertically above the cell at a fixed distance of 40 ± 2 mm from the solution.

The degradation of meldola blue was investigated by monitoring the concentration as a function of time during irradiation of the liquid, analysing samples of the sonicated solution at various time intervals using a Hewlett Packard 8452A diode array spectrophotometer. To maintain the acoustic characteristics of the cell constant,[21] each time a sample was taken, the same volume of meldola blue free solution was added to the cell. Modifications in concentration due to this dilution were taken into account (*ca.* 1%).[9] In order to monitor the production of products from the other reactions studied an electrochemical detection system was employed.[9,23,24] The solutions and acoustic pressure are collected in Table 1. Acoustic pressure measurements were made with a Bruel & Kjaer 8103 hydrophone and a Bruel & Kjaer 2635 charge amplifier. It should be noted that owing to the finite size of the sensing element within the hydrophone in comparison to the spatial pressure maximum, some spatial averaging will occur causing underestimation of the actual value to be obtained.[21,25] Audible airborne noise, emitted from the cell, was detected using a calibrated Bruel & Kjaer 4133 condenser microphone (detecting broadband sound radiation in the audible section of the sonic spectrum) attached to a Bruel & Kjaer 2609 amplifier. The weighting of the amplifier was set to 'A' corresponding to normal human hearing. The microphone was positioned vertically above the cell at a distance of 7.5 cm above the liquid.

In order to measure light emission from the acoustic cells used throughout the results reported here, two experiments were performed. In the first an electrolyte solution (see appropriate figure legend) was irradiated with ultrasound (generating multibubble sonoluminescence, MBSL), while in the second a sodium carbonate solution containing luminol (generating multibubble sonochemiluminescence, MBSCL) was employed. In both cases 100 cm^3 of the respective solution was placed in the cell. Light emission was then measured as a function of frequency. This measurement was achieved by irradiating the solution with ultrasound for 20 s at each frequency employed in the range from 20 kHz to 160 kHz in increments of 1 kHz followed by a 10 s silent period while the frequency was changed for the next irradiation. This is expected to remove hysteresis effects[25,27] due to seeding of the solution from cavitation bubbles produced in the previous ultrasonic irradiation period. During each irradiation of the liquid within the cell the photon counter measured the emission of light per channel (unit of time). The average of 20 measurements was used as the final photon count at a particular frequency (denoted as a subscript on the y axis label).

The cell was thermostated at 25 °C. Heating of the solution during the experiments was found to be relatively small. Typically *ca.* 0.5 °C during initial ultrasonic irradiation of the liquid and <1 °C over 100 s using a temperature probe placed within the cell containing 100 cm^3 of pure water exposed to 125 kHz ultrasound at 100 V drive amplitude.

Table 1 Collection of solution conditions employed and measured spatial 0 to peak acoustic pressures (P)

Figure no.	Reaction	Solution conditions	P/Bar
	Fricke	1 mM $FeSO_4$, 1 mM NaCl, 0.4 M H_2SO_4	2.17@125 kHz
3	H_2O_2	pH 5.5 citrate/phosphate[26]	2.3@124 kHz
	$Cu^{2+}/H^{\bullet}$	10 mM $CuSO_4$, 1.5 M NaCl	2.6@125 kHz
4, 5	Weissler	10 mM KI, 90 mM KCl	[a]

[a] See Fig. 4.

Results and discussion

Light emission from a cylindrical acoustic cell

Fig. 1 shows a plot of the photon count recorded for MBSL and MBSCL as a function of acoustic frequency. The insert in the plot shows an actual set of MBSL data recorded in the range 120–124 kHz. Four major peaks are clearly observed, and in particular the largest emission peak, from 117 kHz to 138 kHz should be noted. It is clear that the light emission for both MBSL and MBSCL occur at approximately the same frequencies within the range studied. However, the photon detection rate from MBSCL is *ca.* 30 times greater.

The degradation of an organic species

In order to test the sonochemical activity of the reactor, five different reactions were studied as a function of ultrasonic frequency. In the first meldola blue (MB) was degraded with ultrasound over the same frequency range as that shown in Fig. 1. The ultrasonic degradation of many organic species has been reported[8,9] and is thought to follow a pseudo first order process.[28] The insert in Fig. 2 shows a pseudo first order plot of the corrected decay of the concentration of meldola blue as a function of time. This linear plot indicates that the ultrasonic degradation of meldola blue also follows apparent first order

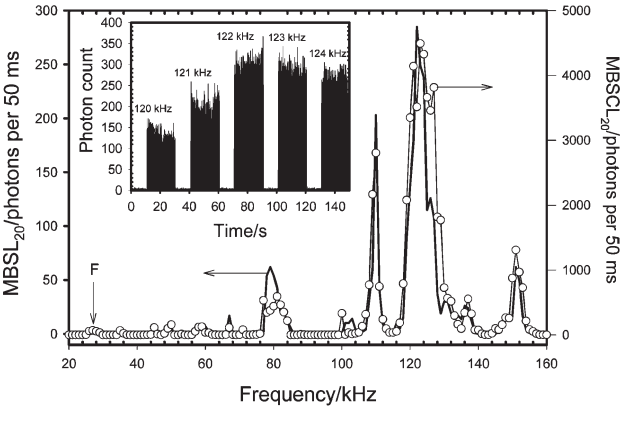

Fig. 1 Plot showing the $MBSL_{20}$ (—) and $MBSCL_{20}$ (—○—) output of the sonochemical cell as a function of drive frequency. A solution containing 50 mmol dm^{-3} Na_2CO_3(aq) or 1 mmol dm^{-3} luminol/50 mmol dm^{-3} Na_2CO_3(aq) was employed respectively. The insert in the plot shows a section of the actual photon count for part of the $MBSL_{20}$ experiment. 'F' denotes the fundamental frequency of the transducer employed.

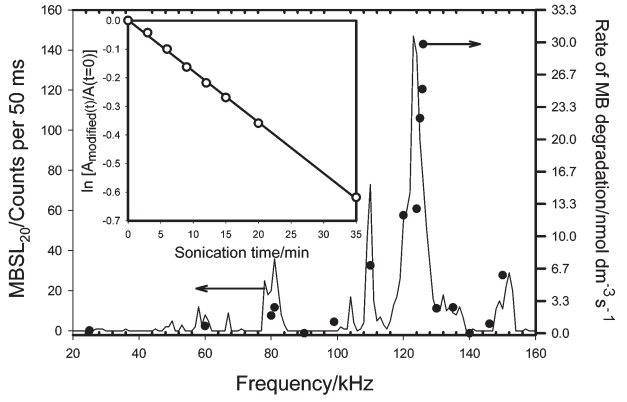

Fig. 2 Plot showing the variation in the rate of the sonochemical degradation of meldola blue (●) and $MBSL_{20}$ (—) output as a function of frequency. The cell contained a 0.1 mmol dm^{-3} meldola blue (degradation experiments only) within an aqueous 10 mmol dm^{-3} HCl and 0.1 mol dm^{-3} NaCl. The insert shows the corrected first order plot for the sonochemical degradation of meldola blue (126 kHz).

kinetics. This process was repeated over a range of frequencies. Fig. 2 shows that the rate was strongly dependent on the ultrasonic frequency, with a change in the rate of several order of magnitude over the entire frequency range studied. Four peaks in the degradation rate and the light emission are apparent (at 80–81, 110, 120–135 and 150 kHz). The correlation between the destruction of meldola blue and MBSL is striking.

Redox radical trap experiments

In order to investigate how the rate of radical production varied as a function of frequency, a variety of reactions were investigated. Fig. 3 shows the variation in the rate of three reactions known to be sensitive to radicals produced through cavitation as a function of frequency compared to MBSL output of the cell over the most active frequency region. Fig. 3 illustrates how sampling in 10 kHz increments in a sonochemical experiment might miss, through aliasing, features (*e.g.* peaks), which are revealed in the 1 kHz resolution luminescence data. In all three reactions investigated there is a remarkable agreement between the reaction rate and the MBSL output of the cell. Both the destruction of an organic and the Fricke reactions are associated with the production of $OH^{\bullet}$ (and other oxidising species generated through cavitation action and subsequent reactions).[16,17] Hence it is unsurprising that hydrogen peroxide will be produced through geminate recombination (see Fig. 3b). However, as well as the production of $OH^{\bullet}$, $H^{\bullet}$ radicals should be generated within the solution. It has been shown, for example by spin trapping experiments, that these species can be detected within a cavitating environment.[12] However, fewer reports of quantitative yields of the $H^{\bullet}$ species can be found within the literature due in part to the competitive pathways for $H^{\bullet}$.[16] It is possible to detect evidence for $H^{\bullet}$ by monitoring the formation of $CuCl_2^-$ electrochemically.[23] Fig. 3c shows the rate of $CuCl_2^-$ production as a function of the ultrasonic frequency employed. Fig. 3c shows a broader response compared to Fig. 3a and Fig. 3b. This may be due to the high NaCl concentration employed.[29,30] This will change the acoustic properties of the cell. In addition sonoluminescence has been shown to be dependent on the ions present within the solution.[31]

Acoustic measurements

Pressure measurements within the liquid phase of a reactor are key to cavitation inception and dynamics.[25] A hydrophone, placed within the liquid, will monitor the time-varying component of the pressure field, which comprises three components,

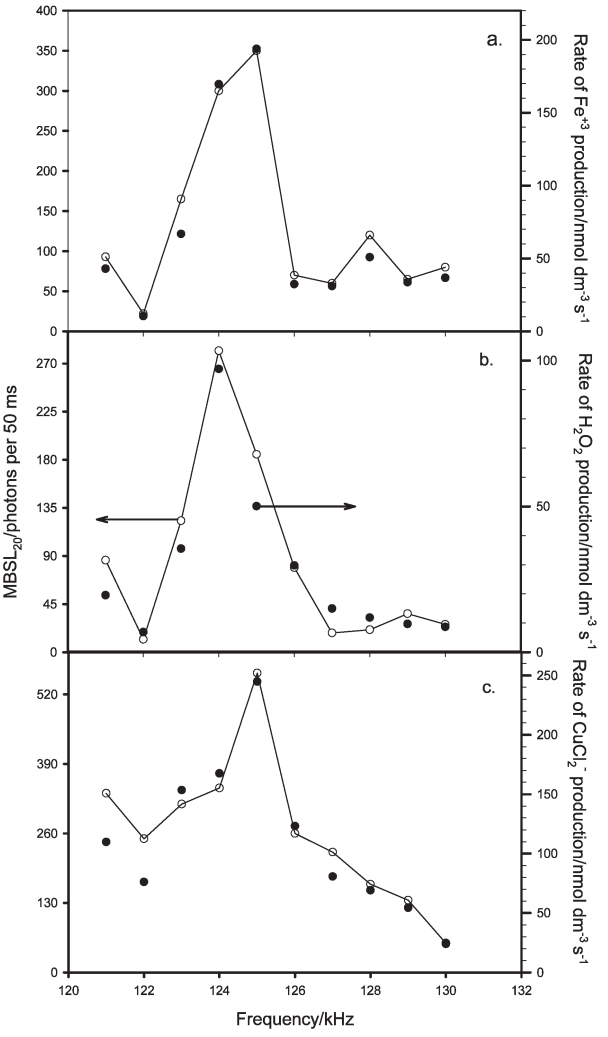

Fig. 3 Plot showing the frequency dependence of both $MBSL_{20}$ output of the cell (—○—) and three sonochemical reactions (●). The solution conditions can be found in the experimental section. The standard deviations associated with these measurements were 7, 6 and 8 nmol dm^{-3} s^{-1} for the Fricke, hydrogen peroxide and copper system respectively.

all of which are inhomogeneous: the applied 'driving' sound field generated by the transducer; the reverberant sound field from reflections in the vessel, and the acoustic and hydrodynamic pressure fluctuations, which result from cavitation. At any given location within the vessel, the amplitude of the driving field will depend on the frequency responses of both the driving transducer and the vessel. This has been shown to be strongly modal for the vessel used in this paper.[21] As a result, the driving acoustic pressure amplitude exhibits spatial maxima and minima. This implies that measuring the 'power or intensity' of a cell or driving at the transducer fundamental (F) will have little relevance. This is because, even if it reflects the acoustic power and not simply the electrical rating of the transducer, it is a spatially averaged quantity. Cavitation responds to local pressures, and hence this is the measure that should be employed in inhomogeneous sound fields, where spatially averaged measures are inappropriate.[25] The sound field is frequency-dependent, so that as one moves to higher frequencies one tends to obtain more rings, of increasingly narrow thickness and spacing.[21] Hence it is difficult to predict what effect a changing modal structure will have on a photon counter, which exhibits a finite 'footprint'. For this study the *a priori* issue to be investigated is whether, if the footprint is sufficiently large (here the photon detector counts over the whole cylinder), the photon count will in general follow the

amplitude of the driving field within the cylinder. The acoustic pressure amplitudes from three points within the cell are shown in Fig. 4. These data show that the pressure measured within the cell not only follows the transducer resonance (F) but also has the pressure components contributed by transducer harmonics and the reverberant modal sound field. This can be seen as a series of pressure peaks within Fig. 4, varying with the position of measurement. There is a pressure maximum in the region of 120–130 kHz, which is the same frequency region as the luminescence maxima and reaction rate maxima recorded for the same cell and shown previously (see Fig. 1). However, the pressure maxima shown in Fig. 4 at lower pressures do not coincide with high reaction rates. Only luminescence appears to predict where reaction rates will be highest. It can be deduced that pressure measurements, at a few local points within the cell, cannot be relied on to predict at what frequencies all high sonochemical reaction rates will be observed (as these may occur away from the hydrophone position).

Fig. 5 shows how the recorded broadband audible noise produced by the cell varies as a function of the ultrasonic driving frequency. In this case the highest audible acoustic output occurs when the cell is driven at 27 kHz, which coincides with the fundamental of the transducer. However, if we compare the acoustic emission to both MBSL and the rate of organic destruction (see Fig. 1 and 2) then it is clear that high audible acoustic emission does not predict where the highest rates or luminescence are observed. This is surprising as the high acoustic audible emission indicates that there are large amounts of transient (inertial) cavitation within the cell.

Discussion

The results reported here suggest that the study of discrete frequencies over a wide frequency band may produce misleading results. Neglect of the dominant cause of frequency-dependence (the transducer/cell) is commonplace. The complete system that must be considered is shown in Fig. 6. These components have frequency dependences to a greater or lesser extent. It should be noted that if the acoustic pressure field within the vessel is mapped, none of these dependences need be known bar that of the detector. Mapping the field (with sufficient spatial resolution) is not a difficult task when there is no cavitation, but it is time consuming, and often a measurement of the spatial peak pressure is adequate (*e.g.* for threshold measurements). However, in many sonochemical studies no acoustic pressure measurements are taken, and in such circumstances the frequency dependences of the various components needs to be considered (not just the resonance quoted by the manufacturer‡ (F)). However, in studies where the frequency dependence of a reactor is to be studied, keeping to a resonance is not an option. Even if the driver has multiple resonances and measurements are restricted to these, the acoustic pressure field needs to be measured not only because the Q factors and efficiencies of the different transducers will likely differ, but also because the spatial inhomogeneity of the modal sound field must be reconciled with the spatial averaging inherent in the detector system. Whilst ignoring the frequency dependence of the signal generator and power amplifier does not often lead to great error, neglect of the frequency dependence of the reverberant field and the transducer is to ignore the two most important frequency dependences in the system. It is suggested that statements claiming 'the optimal frequency' for sonochemistry in general are to be avoided. As cavitation is a non-linear threshold phenomenon, maintaining the same 'power/volume ratio' is misleading as it is the spatial peak (and not spatially averaged) acoustic pressure, which will be important for cavitation inception. Indeed as the modal character of the sound field changes, so too does the volume of the reagent, which is exposed to cavitation (*e.g.* see ref. 21 Fig. 11, which shows that only a portion of the sample volume luminesces and that volume will change with frequency). It is suggested that the threshold for inertial cavitation, which exists in pressure/radius/frequency space, and also the consequences of differing bubble populations within the liquid be considered.[25,32–35] Comparison of chemical rates and cavitation activity requires consideration of the time dependence involved. Chemical rates are always quoted as a 'per second'

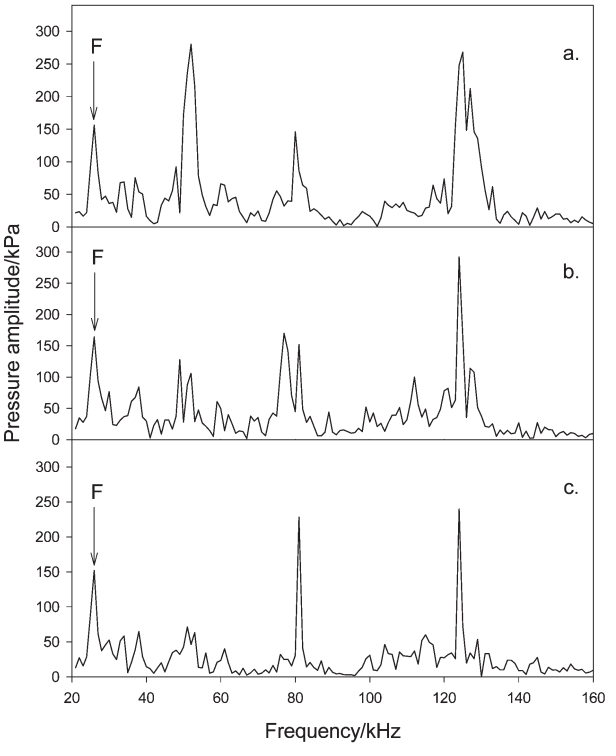

Fig. 4 Plot showing the variation in acoustic pressure amplitude recorded in three positions in the cylindrical reactor as a function of acoustic frequency. The hydrophone was positioned *ca.* 1.5 cm from the base of the cell. 'a', 'b' and 'c' represent the hydrophone in the centre, 1 cm off centre and next to the wall respectively.

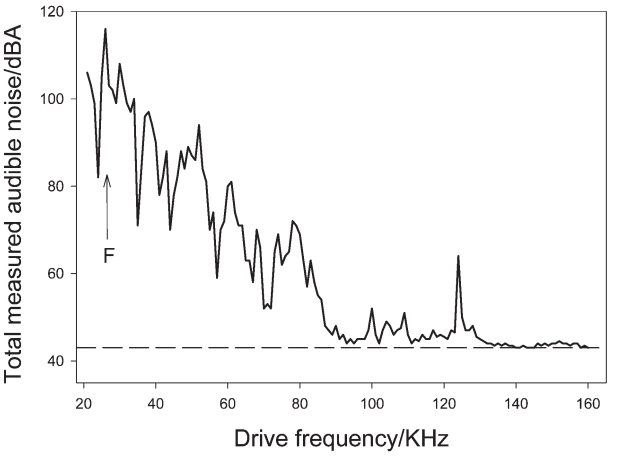

Fig. 5 Plot showing the variation in the measured audible noise produced by the cell employed as a function of ultrasonic frequency. (---) indicates the measured background noise within the lab in the absence of ultrasonic irradiation of the liquid.

‡ Some commercial systems rely on electrical matching of the transducer to the amplifier. Although this leads to a high-energy transfer to the transducer it does not necessarily correspond to a high resonance of the cell.

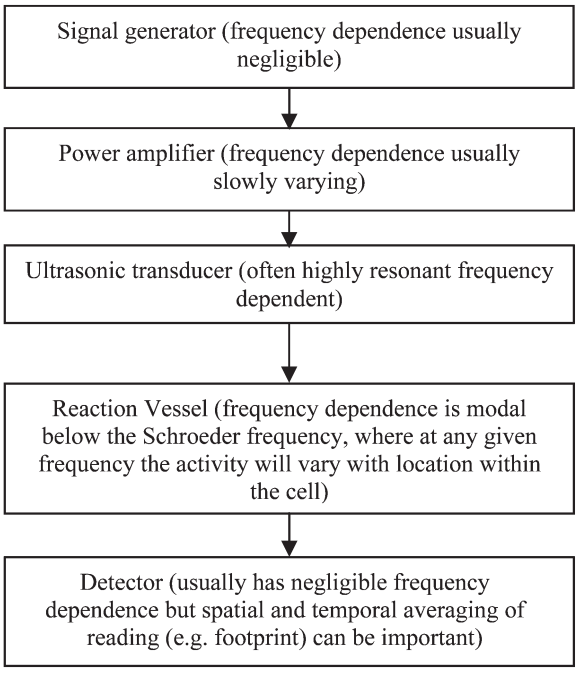

Fig. 6 Diagram showing the components and their various frequency dependences commonly employed in sonochemical experiments.

measurement. There will clearly be more opportunities to generate cavitation events at higher frequencies compared to lower frequencies in the 'per second' sense. It must also be remembered that as the frequency is increased the cavitation threshold will rise and for a given bubble population there would be less inertial cavitation.[25] It is also interesting to note that in the majority of cases studied, the rates of reactions seem to have been solely focussed on rich radical chemistry. This does not address directly the question of reactions that are driven within the gas phase of the bubble.

Lastly the measurements of pressure, and to some extent light output of the cell, will depend on the ability of the particular sensor employed to act as either a point sensor or a global sensor. In the case of pressure measurements, the hydrophone employed will only sense the pressure variations at the point within the liquid that it is placed. If the cell has a strong spatial variation in pressure, as it will below the Schroeder[21] frequency, then these types of measurement will be inadequate in determining the overall performance of the cell.

Conclusions

The results reported in this paper demonstrate that it is possible to measure accurately and quantitatively the rates of a variety of reactions over a varying frequency range (20–160 kHz) under controlled physical and acoustic conditions. These studies show that the rate of reactions can be measured to the nmol dm^{-3} s^{-1} level. The light output from the sonochemical reactor was measured for both MBSL and MBSCL. The maximum rates of the reactions studied were observed at frequencies that did not coincide with the fundamental of the ultrasonic transducer employed. Indeed the rates follow the modal pattern of the reverberant field. In this study MBSCL or MBSL predicted the optimum rate for a given ultrasonic reactor. No strong conclusions on the variation of luminescent output with frequency should be drawn, as these may be complicated by other factors (*e.g.* cell resonance, transducer amplitude and transducer efficiency). Most importantly, it is recommended that the sound field in the vessel be characterised with fine frequency resolution around the test frequency. Attention must be paid to detuning between the driving field and the mode (for example as a result changes in the liquid composition, temperature, volume or bubble population).[21]

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