Coventry University

DOCTOR OF PHILOSOPHY

The effect of ultrasound on organic synthesis and processing from laboratory to large scale

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Award date:
1993

Awarding institution:
Coventry University

Link to publication

THE EFFECT OF ULTRASOUND ON ORGANIC SYNTHESIS AND PROCESSING FROM LABORATORY TO LARGE SCALE

by

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Submitted for the Degree of
Doctor of Philosophy
at
Coventry University
Division of Chemical Sciences

ACKNOWLEDGEMENTS

I would like to thank Prof.T.J.Mason and Dr.J.P.Lorimer for their invaluable guidance, advice and encouragement throughout the duration of this work.

Thanks also to all the staff at Coventry University for their help and humour throughout the years and for helping to make my time here an enjoyable experience.

In addition to this I wish to acknowledge Fison's Pharmaceuticals who supported the first part of this project and specially thanks go to Dr.A.R.Harris and Dr.P.W.Wright. I would also like to thank Mars Confectionery for the sponsorship of the second part of this research programme and special thanks to Dr.J.Meyer and F.Earis for their support and technical advice throughout this project.

Last but definitely not least I would like to thank Stef for always being there.

ABSTRACT

The research programme involved the exploitation of ultrasound with a view to applications within commercial and processing industries.

This was accomplished by employing dosimetry and calorimetry to study the efficiency of several sonochemical reactors. The effect of factors such as reaction vessel geometry and volume was investigated and the general trends obtained for all three dosimeters were comparable.

The effects of various parameters *e.g.* power, solvent, volume etc etc on the sonochemical O-alkylation of 2,6-dimethylphenol was examined. Decreases in temperature and volume, and increases in concentration and power, led to increases in the sonochemical effect.

A study of the alkylation products from a reaction between 5-hydroxychromone-2-carboxylic acid ethyl ester with less reactive alkyl halides such as 1- and 2-bromobutane resulted in comparisons with phase transfer catalysis and conventional thermal methods.

An investigation of the dehydrogenation of tetrahydronaphthalene under the influence of sonication was also attempted. Dehydrogenation was enhanced by sonication with sonochemical dehydrogenation occurring 20-40°C below the corresponding thermal reaction.

Sonication as a processing aid was studied using examples taken from the food industry. The applications of particle size reduction, emulsification and crystallisation of various foodstuffs such as rice, sugar and cocoa grains were examined. The effect of sonication on the viscosity of gelled starch was also monitored with a view to achieving either a permanent or temporary reduction in viscosity.

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CHAPTER 1

SONOCHEMISTRY

THEORETICAL AND PHYSICAL ASPECTS

1.0 SONOCHEMISTRY - Theoretical and Practical Aspects

The interest generated about the field of ultrasonics is still escalating. More and more chemists are coming around to introducing simple ultrasonic equipment into laboratories. New better designed and more widely applicable equipment is now being produced both for large and small scale work.

The field of ultrasonics is widespread throughout many different disciplines such as Engineering, Medicine, Biology, Building and Plastic Welding. A study of the use of ultrasound within chemistry is known as SONOCHEMISTRY and it is in this area that this project is based.

The present author's research programme was comprised with a view to exploiting the use of ultrasound within the commercial sector and a variety of processes relevant to industry and capable of scale-up were studied. With this view in mind we examined the efficiency of several laboratory sonochemical reactors employing iodometry, the Fricke dosimeter (Fe^{2+} -> Fe^{3+}) and calorimetry. An attempt was made to examine the fundamental factors affecting sonochemical reaction processes and for this investigation the O-alkylation of 2,6-dimethylphenol by an alkyl halide in the presence of base was examined. The effect on reaction efficiency of changing parameters such as power and temperature was investigated. Sonication was also compared to other laboratory procedures for the enhancement of alkylation, such as phase transfer catalysis and conventional thermal methods.

Although sonochemical hydrogenation has been well documented the exploitation of sonochemical dehydrogenation has been somewhat limited. An investigation of the dehydrogenation of tetrahydronaphthalene under the influence of sonication was undertaken in order to examine its effects on catalyst activation.

Examination of sonication as a processing aid using examples taken from the food industry was attempted. This involved an assessment of the problems involved in the scale-up of sonicated processes. This was targeted at typical processing applications such as particle size reduction, emulsification and crystallisation of various foodstuffs.

Due to the diversity of the processes examined the relevant theories and literature regarding the process under study will be discussed in the individual chapters. However in order that the basic principles of ultrasound are understood these are introduced separately.

SONOCHEMISTRY - Basic Principles

1.1 TRANSIENT AND STABLE CAVITATION

Ultrasound waves have a frequency of >16kHz. The upper limit is thought to be 5MHz for gases and 500MHz for liquids and solids[1]. The sonic waves are usually introduced into the system via a rapidly vibrating "body" such as a sonic horn (see later). A series of compression and rarefaction waves are formed. These waves are longitudinal within liquids and gases. Varying pressures within the liquid at ultrasonic frequencies induce the formation of cavitation bubbles, the sources of sonochemistry. During the rarefaction cycle microbubbles are formed which can become filled with the gases usually present in the solvent (e.g. air, solvent vapour).

There are two types of cavitation bubbles Transient and 'Stable' bubbles.

Transient bubbles often collapse within the following compression cycle. Vapour diffusion into the bubble causes it to increase to almost twice its original size. The bubble becomes unstable and collapses violently into smaller bubbles which, if small enough, may redissolve or act as nuclei for further bubble growth. Transient bubbles are so short lived that it is thought that dissolved gases have no time to diffuse into the bubble cavity.

Stable bubbles, so named because they are longer lived than transient bubbles, exist through several compression/ rarefaction cycles simply oscillating at resonance frequency. Once mass transfer becomes unequal and dissolved gases diffuse faster into the bubble than out (via rectified diffusion[2]) it begins to grow. Two options are now available the stable bubble may become transient and collapse, with a slightly weaker implosion than 'normal' transient bubbles due to the 'cushioning' effect of diffused gases, or it can continue to grow until it eventually rises to the surface and bursts, thus effectively degassing the solvent.

1.2 EXAMINATION OF T_{max} AND P_{max}

1.2.1 The case for Transient cavitation

Various authors such as Noltingk and Neppiras[3], Flynn[4] and later Neppiras alone[5] have produced calculations which indicate the presence of very high temperatures and pressures within cavitation bubbles.

Due to the very fast bubble vibrations any heat generated within the cavity cannot be dispersed to the surrounding medium. During the compression cycle these temperatures and pressures are increased to many thousands of degrees and atmospheres prior to bubble collapse. On collapse these temperatures and pressures are released into the surrounding medium and many effects observed due to sonication may be explained by this extremely violent collapse.

Under adiabatic conditions T_{max} and P_{max} may be calculated.

$$T_{max} = T_O \left[\frac{P_M (\gamma - 1)}{P} \right]$$

$$P_{max} = P \left[\frac{P_M (\gamma - 1)}{P} \right]^{\gamma / \gamma - 1}$$

T_O - Liquid ambient temperature.

P_M - Liquid pressure at transient collapse.

P - Pressure within the bubble at maximum size (taken to be vapour pressure of liquid (P_V) or P_V and P_G if gas has also entered the cavity).

γ - Ratio of specific heats of gas (gas/vapour mix).

T_{max} and P_{max} are found to be highest for monoatomic and diatomic gases due to the large value obtained for (γ - 1) thus the most efficient cavitational effects are obtained.

By observing the rate at which chemical reactions take place Suslick and co-workers[6] calculated the temperatures and pressures within cavitation bubbles. The gaseous contents within the cavitation bubble reached 5,500°C and the immediate surrounding liquid reached 2,100°C. The pressure within the cavitation bubble was estimated to be approximately 500 atmospheres. The maximum temperature and pressure reached is dependent upon many factors such as reaction temperature, solvent employed and type of dissolved gases present this may be demonstrated as follows:-

It is possible to estimate the temperatures and pressures of a cavitation bubble by studying sonoluminescence spectra. Sehgal and Verrall[7] examined the peak shifts and bandwidth broadenings of spectra of aqueous solutions containing potassium or sodium salts. Cavitation bubble temperatures and pressures were calculated as 3,400K and 310 atmospheres respectively. However when the spectra of aqueous solutions saturated with nitrogen monoxide and nitrogen dioxide were examined cavitation temperatures of only 1350K and 860K respectively were observed. This corresponds to the theory that lower cavitational effects are observed with gases of higher atomicity (see earlier).

1.2.2 The case for Stable cavitation

Stable cavitation bubbles in resonance with the ultrasonic field also produce high temperatures and pressures as calculated by Fitzgerald et al[8].

$$T_O / T_{MAX} = [\, 1 + Q \times [\, (P_h / P_m)^{1/3\gamma} - 1] - 1]^{3(\gamma - 1)}$$

P_h - Hydrostatic pressure.

P_m - Acoustic pressure amplitude in the liquid

Q - Damping factor (ratio of resonance amplitude to static amplitude of the oscillating bubble).

At the high temperatures and pressures present within cavitation bubbles it is not surprising to find high energy species forming and subsequent interactions result in Sonoluminescence.

1.3 SONOLUMINESCENCE

The weak emission of light seen in some cavitating liquids is known as sonoluminescence. Sonoluminescence is present as liquids are subjected to forces such as shock waves, lasers and ultrasound. Light is thought to be emitted as the high concentration of energy within a cavitation bubble is released in a short space of time.

Two theories exist in an attempt to explain this phenomenon. The thermal theory and the electrical theory.

1.3.1 Thermal theory

This is based on the 'hot spot' theory of Noltingk and Neppiras[3] in which the high temperatures produced on adiabatic compression of the cavitation bubble result in the formation of excited atoms and radicals. Sonoluminescence occurs as these excited molecules either enter lower energy levels and thus release their stored energy as light emissions or light emissions occurring due to recombination of the radicals in the cavitation bubble.

1.3.2 Electrical theory

A new theory has recently been proposed by Margulis[9] in which many factors previously unexplained by the thermal theory have been overcome. It proposes the formation of large deformed bubbles from which smaller bubbles form and detach themselves. It is thought that the electrical charge accumulated on the larger bubble is concentrated on the smaller bubble surface as it grows. Unable to diffuse the charges this results in an electrical discharge to equalise the surface charges and is thought to be an electrical example of sonoluminescence and also accounts for electrical pulses observed in liquids.

Sonoluminescence spectra of distilled water containing noble gases give a peak at 310nm corresponding to excited hydroxyl radicals and a broad spectrum extending from 240nm to the near infra-red[7]. Addition of electrolytes such as nitrate and sulphate ions alters the broad band continuum observed for pure water. It is thought that interactions between the electrolytes and hydrogen and hydroxyl radicals and ions, formed on sonication of water, result in the production of new species.

Addition of metal ions to distilled water results in light emissions characteristic of the corresponding metal. Potassium salt solutions give emission peaks corresponding to the first excited transition state of potassium.

Sehgal et al[10] obtained light spectra on sonicating a sample of distilled water saturated with various gases. The spectra obtained give a range between 240nm to the near IR region. It appears that intensity increases with an increase in the relative molecular mass of the gas. It is thought that emissions from transient bubbles are due to the excited states of water, hydroxide, hydrogen or oxygen molecules. Emissions from stable bubbles are thought to come from the recombination of hydrogen and hydroxide radicals due to the lower temperatures present.

$$H^{\cdot} + OH^{\cdot} \quad -> \quad H_2O + hv_2$$

It has been assumed that noble gases do not undergo interaction with the excited atoms and molecules however this is not the case for liquids saturated with air, oxygen or nitrogen. In the case of nitrogen excited species of nitrogen dioxide are observed at high temperatures.

Aqueous solutions saturated with nitrogen dioxide and nitrogen monoxide show emissions corresponding to an excited nitrogen dioxide molecule in the gas phase[11] thus indicating that sonoluminescence occurs in the same phase, that is within the gaseous vapours of a cavitation bubble.

Whatever the correct interpretation cavitation does result in the following types of reactions.

1.4 CAVITATIONAL EFFECT

It is thought that cavitation affects the reaction medium in these possible ways.

1) Interactions occurring within the cavitation bubble itself (radical formation, sonoluminescence). Homogeneous reactions (liquid/ liquid).

2) Interactions occurring at the bubble interphase (aiding initiation of polymerisation).

3) Interactions within the liquid medium due to the high temperatures and pressures released at bubble collapse (polymer degradation, catalyst activation and phase transfer catalysis). Heterogeneous reactions (solid/liquid).

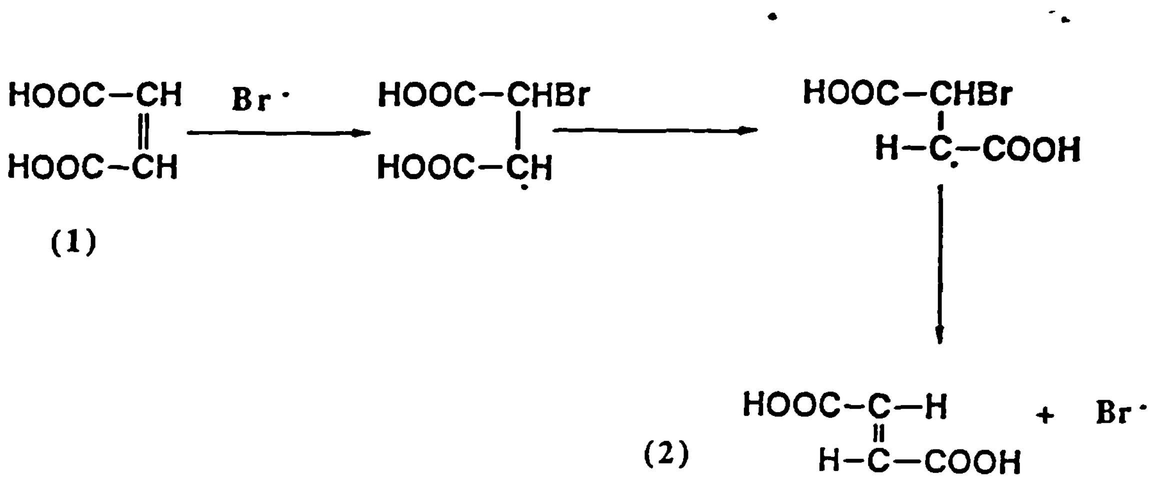
1.4.1 Radical formation within the cavitation bubble

Elpiner et al[12] have produced results which confirm the dissociation of initiators within the cavitation bubble. The formation of atoms and/ or radicals due to the high temperatures and pressures present during adiabatic bubble compression can result in the initiation of chain reactions.

The example given is the isomerisation of maleic acid (1) to fumaric acid (2) in the presence of a catalytic amount of bromine initiator. During sonication bromine radicals are formed which combine with the cis-isomer going on to rearrange to the more stable trans-isomer.

It is thought that the bromine radicals are formed within the cavitation bubble but interact with the cis-isomer at the bubble interphase (the isomer not being volatile enough to enter the bubble itself). The presence of oxygen inhibits the reaction by forming intermediate peroxide compounds also at the interphase.

$$Br_2 \longrightarrow 2Br.$$



H radical and OH radical formation due to ultrasound has been positively identified by ESR measurements[13]. They are now believed to be formed through thermal dissociation of water molecules in the temperatures within the cavitation bubble. Radicals within the bubble are often compared to those obtained in combustion or shock tube treatments[14].

Sonolysis of water in the presence of deuterium results in the following[15]:

$$D_2 + H_2O \rightarrow HD + HDO$$

Under pure argon hydrogen and hydrogen peroxide are formed, (with small amounts of oxygen), when water is sonicated as follows:

$$H_2O \; -> \; H^{\cdot} + OH^{\cdot}$$

$$H^{\cdot} + H^{\cdot} \; -> \; H_2$$

$$OH^{\cdot} + OH^{\cdot} \; -> \; H_2O_2$$

Some recombination of hydrogen and hydroxide radicals also occurs returning to water.

It was also shown with increasing levels of deuterium the amount of peroxide formed decreases thus indicating the scavenging of hydrogen and hydroxide radicals by deuterium.

Cavitation may be induced in alkanes leading to C-C bond cleavage and radical formation[16]. On sonication of n-alkanes a mixture of hydrogen, methane, ethane and the smaller alkenes is produced.

Sonication results in C-C bond cleavage leading to radicals and further still ethylene elimination to give shorter chain radicals. Addition of diphenylpicrylhydrazyl, a radical trap, confirms the presence of radicals by completely inhibiting the formation of hydrogen, methane, ethene etc etc.

1.4.2 Polymerisation - at the bubble interface

Kruus[17] reports a series of experiments explaining a range of polymerisations induced by ultrasound.

Polymerisation with bromobenzene is thought to be initiated by dissociation of the weakest bond, in this case the C-Br bond. The subsequent formation of free radicals results in the initiation of polymerisation with a darkening of the solution occurring.

Sonication of isoprene is thought to give a conjugated system of 8-10 carbons with longer molecules becoming degraded via the C-C bond.

Methyl methacrylate produced the most interesting results in which a significant viscosity increase is observed with the resultant polymer precipitating out on addition of methanol. The average molecular weight of the polymer was 500,000 compared with over 2,000,000 for a thermally initiated polymerisation indicating the occurrence of some polymer degradation.

Cavitational effects outside the cavitation bubble

1.4.3 Depolymerisation

On collapse the cavitation bubble releases its stored up energy which passes through the surrounding medium like a shock wave, strong enough to degrade polymers by rupturing bonds in the main chain.

A common method of following polymer degradation is to measure the solution viscosity from which the polymer weight can be determined. Henglein[18] followed the aqueous degradation of a series of water soluble polymers. A reduction in viscosity, indicating degradation, was obtained for samples of polyethylene glycol, polymethacrylic acid and polyvinyl pyrrolidone amongst others. Carbon monoxide appeared to be the major gaseous product of polymer degradation with some carbon dioxide and methane also observed. The yield of carbon monoxide appears to level off and decrease with solutions containing high concentrations of polymer. The high viscosity of the polymer samples at these concentrations is thought to result in less efficient cavitation and therefore less degradation.

Degradation of polymer samples may also be followed by the use of a radical scavenger. Employing this method Allen et al[19] examined the degradation of dilute solutions of polystyrene, polymethylmethacrylate and polyvinyl acetate.

α, α'-diphenylpicrylhydrazyl absorbs in the red region of the visible spectrum and its consumption may be followed by colorimetry. For every polymer bond broken 2 radicals are produced and 2 molecules of the radical scavenger are consumed. Polymer radical recombination is also suppressed and therefore the rate of polymer degradation should be increased.

1.4.4 Catalyst activation

Pitting at the surface is thought to be due to cavitation bubble implosion on or near the surface of the catalyst[20].

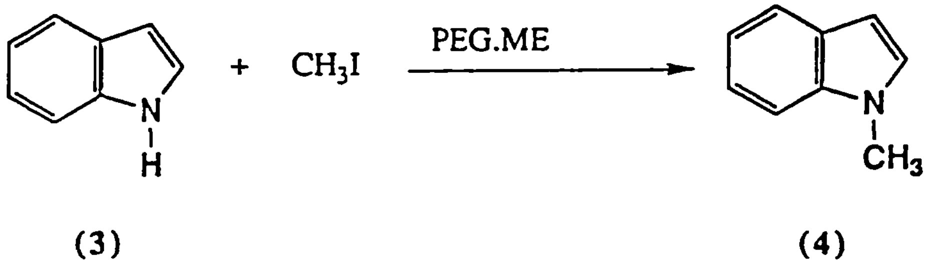
Formation of microjets due to cavitation bubble collapse near the surface of the catalyst results in small jets of solvent being propelled at high speed towards the catalyst surface and pitting it[21]. This is thought to remove the surface reactants and expose further clean catalyst.

Ultrasonic preparation of catalysts is so effective that it is possible to produce metal powder catalysts effective enough to rival Rieke powders. Boudjouk[22] made a series of such catalysts by simple reduction of the corresponding metal halide.

One example of the advantages of sonication when applied to heterogeneous reactions is given by the Ullmann coupling reaction[23]. The Ullmann coupling reaction normally requires large excesses of copper powder. Introduction of sonication to the coupling of 2-iodonitrobenzene reduced the reaction time from 48 hours, with 10 fold excess of copper, to 2 hours with only 4 fold excess of copper.

1.4.5 Phase transfer catalysis

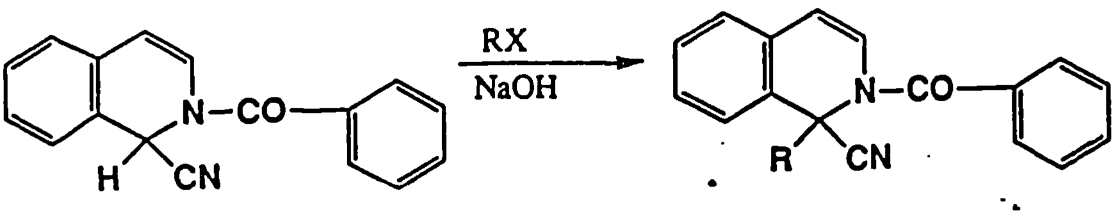
The N-alkylation of amines under solid/ liquid phase transfer catalysis conditions was studied by Davidson et al[24]. High yields of the N-alkylated product (4) were obtained with reduced reaction times in the presence of ultrasound. For example the N-alkylation of indole (3) with iodomethane and polyethyleneglycol methyl ether as phase transfer catalyst, resulted in 63% conversion in under 1/2 hour in the presence of ultrasound and 60% after 5 hours with simple stirring. Indole N-alkylation with benzyl bromide and polyethyleneglycolmethyl ether resulted in 80% conversion after 8 hours stirring and 95% after only 2 hours sonication.



No reaction occurred in the absence of a phase transfer catalyst. Increased mass transfer from ultrasonic streaming is thought to aid the phase transfer reaction.

A similar reaction was examined by Ezquerra and Alvarez-Builla[25]. The alkylation of an isoquinoline Reissert compound (5) was attempted.

No reaction occurred in the absence of a phase transfer catalyst, even in the presence of sonication, indicating that this is a true phase transfer. Sonication of the phase transfer reaction resulted in rate enhancement over the corresponding stirred reaction in most of the alkylation reactions attempted.



(5)

1.5 ULTRASONIC GENERATORS[26]

Generators are the source of ultrasonic energy. There are two types of generators:

1) Mechanical generator, such as the whistle reactor.

2) Electrical generators which need a transducer to convert the electrical energy to acoustic energy.

1.5.1 MECHANICAL GENERATORS

These generators have no need of a transducer being able to produce ultrasonic energy directly. The basis behind the whistle reactor involves a high speed stream of gas or liquid passing over a steel plate which vibrates at ultrasonic frequencies.

Ultrasonic sirens operate by the means of two discs. One disc, with 100 teeth cut into it, rotates at high velocity. The other disc, with 100 holes in it, remains stationary. Compressed air is passed over the discs and the compressions and rarefactions produced as the teeth and holes interact with the air flow produces an ultrasonic wave. The frequency of ultrasound is dependent upon the speed of the rotating disc.

1.5.2 ELECTRICAL GENERATORS

Transducers convert one form of energy to another. Transducers used within ultrasonic equipment are either magnetostrictive or piezoelectric.

Magnetostrictive transducers

Certain ferromagnetic substances, substances which become magnetised when subjected to a magnetic field, exhibit magnetostrictive qualities. Magnetostriction is the alteration of the size of the material as the substance is magnetised. The most common magnetostrictive transducers in ultrasonics are nickel and some ferrites. The substance is usually fashioned into a core of laminated material surrounded by a solenoid coil which carries an AC current allowing the core to vibrate with the variations in current.

Piezoelectric transducers

Piezoelectricity, the conversion of mechanical energy to electrical energy by piezoelectric crystals, was discovered by Pierre Curie in 1880. The most common piezoelectric substances in ultrasonics include quartz, used most often in medical equipment, however barium titanate, lead zirconium titanate and other titanates are the most common for ultrasonic applications. The titanates have to be specially processed and polarised before use. However they can be fashioned into a variety of shapes and can be polarised in any direction thus allowing vibrations of the crystal to occur in the desired direction on the application of an electric current.

Both types of transducers suffer from the problem that they become denatured with heat as the polarity within is broken down. The point of this loss of transducer character is known as the Curie point. As temperatures near this point transducer efficiency is reduced. There is always some power loss within the system and efficiency may be calculated as follows:

$$\textbf{Efficiency (\%)} = \frac{P_{OUT} \times 100}{P_{IN}}$$

An amplifier is needed to increase the transducer signal. The amplifier is usually termed the probe or horn (see later).

1.5.3 Resonance/ Amplitude

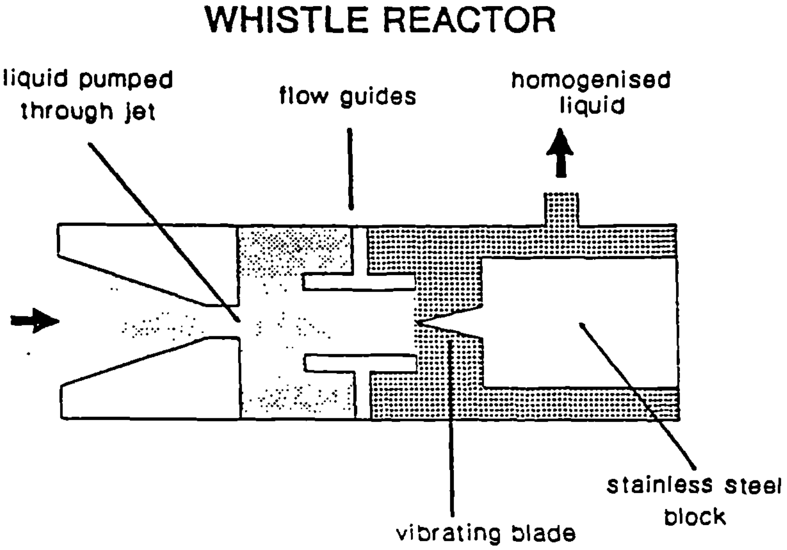
Transducers can change electrical energy to mechanical energy at a wide range of frequencies. However the transducer will vibrate at a much higher amplitude when the generator produces a frequency at which it is mechanically resonant. The resonance point depends upon the size of the transducer and the type of material it consists of.

Often the transducer may not be resonant at a desired frequency and a drop in efficiency and power output occurs thus requiring amplification. This problem is overcome by the production of a composite transducer. This consists of a slice of transducer material being cemented or bolted between two steel plates causing the whole material to vibrate on application of an electric current. By varying the thickness of the front and back plates the resonance frequency of the composite transducer may be altered and vibrations at the desired frequency are amplified. Further amplification may be achieved by the use of tapered extenders and other such devices.

1.6 ULTRASONIC EQUIPMENT[27]

1.6.1 Whistle reactor

The whistle reactor has a simple design. A pump forces a jet of high speed liquid over a steel plate causing it to vibrate at ultrasonic frequencies forming cavitation within the liquid.

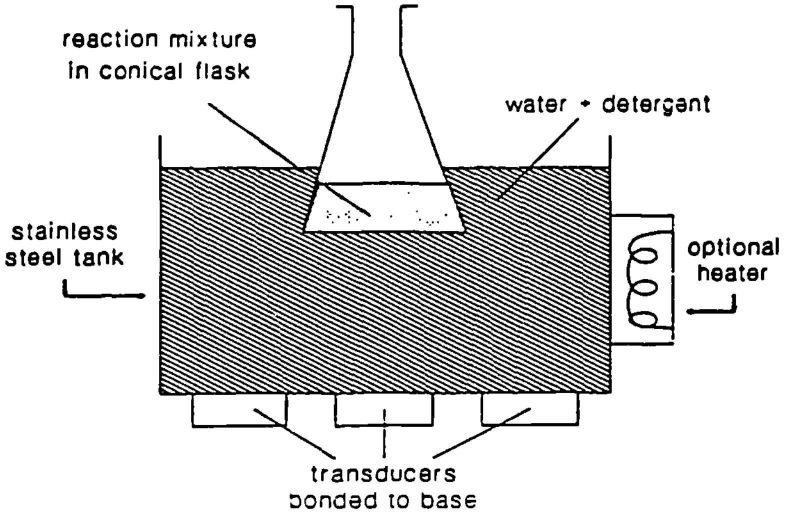


It is used in industry for emulsification of liquids producing substances such as mayonnaise and is also used for defoaming and degassing of liquids.

1.6.2 Cleaning bath

Mason et al[28] give an account of the advantages and disadvantages of attempting sonic reactions with a cleaning bath, also giving examples of the work possible. The cleaning bath is a stainless steel tank with transducers fitted beneath the base. It is readily available and very economic to buy. Although reactions may be performed directly in the bath, due to possible contamination from wall erosion, glass reaction vessels are normally used. Specially designed glassware is not needed as normal laboratory glassware may be used.

DIAGRAM OF A SONIC BATH SYSTEM



One of the major disadvantages of attempting reactions in a cleaning bath is that the amount of energy entering the reaction vessel is only approximately 1 - 5 Wcm^{-2} [29]. The bath transducers are situated underneath the base of the bath and the sonic waves have to pass through the bath medium, usually water, and then the reaction vessel walls before entering the reaction mixture.

The depth and position of the reaction vessel are also important and have to be reproduced if a series of reactions are to be attempted. To achieve maximum power input the vessel must be placed over a transducer and at a depth corresponding to a multiple of half the sonic wavelength, at the point of highest wave amplitude.

Temperature control is also limited. As the bath operates the bath medium heats up.

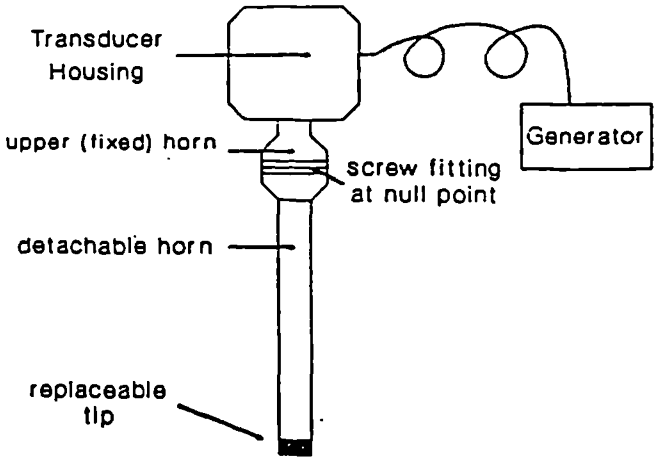
Any attempt at cooling via addition of ice or a flow of liquid in and out of the bath will disrupt the wave pattern and reduce the amount of energy penetrating into the carefully positioned vessel. Thermostatted baths are available but these operate assuming water to be the bath medium and therefore reaction temperatures of only upto 100°C are possible.

Submersible transducers are now available enabling any vessel to be converted into a sonic bath.

1.6.3 Sonic horns

Often referred to as sonic probes these offer the advantage of allowing a much higher power input into the reaction system as they are directly immersed in the reaction mixture. The amplitude of the power can be increased by the use of tapered extenders attached to the horn, the transducer material being contained in the horn. The power applied to the system may also be controlled.

DIAGRAM OF A PROBE SYSTEM



The temperature within the reaction vessel may be controlled by immersing the vessel into an ice bath or a suitable thermostatted bath. The disadvantage of this system is that horn tip erosion occurs and the reaction mixture becomes contaminated with metal particles. Many horns now employ studs which are screwed onto the tip and as these screws become eroded they are able to be replaced thus saving on the cost of replacing the complete horn.

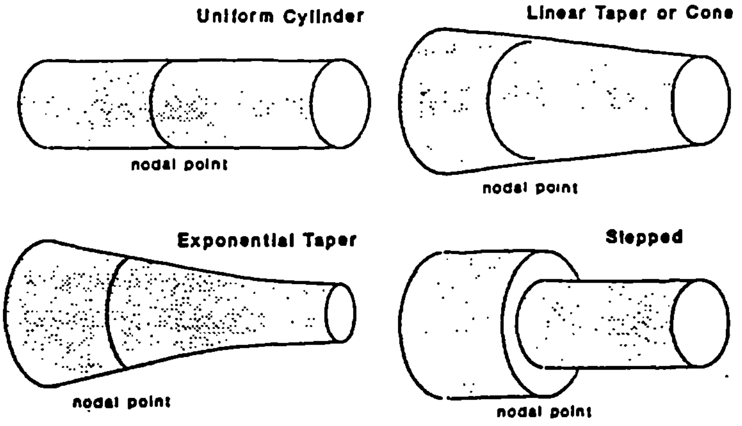
The probe systems employ fixed frequency, usually 20kHz, however a new system has been developed, the Undatim equipment, where the frequency generated may be changed by simply altering the horn used.

1.6.4 Horn extenders

Several types of extenders are available and are used to amplify power intensity.

Linear tapered extenders amplify the power output 4 - fold but exponentially tapered extenders amplify this amount further still.

HORN SHAPES



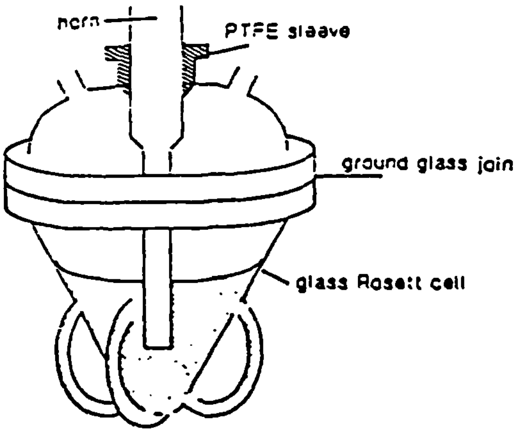
Extenders are usually made of titanium alloy and are of a length corresponding to a multiple of half a sonic wavelength.

The cup horn employs a probe generator with a specially adapted transducer horn which tapers outwards instead of inwards. With a special cup screwed to the top and filled with water it acts as a very powerful sonic bath. The disadvantage of this system is that the reaction vessels are very small thus only small scale reactions can be performed.

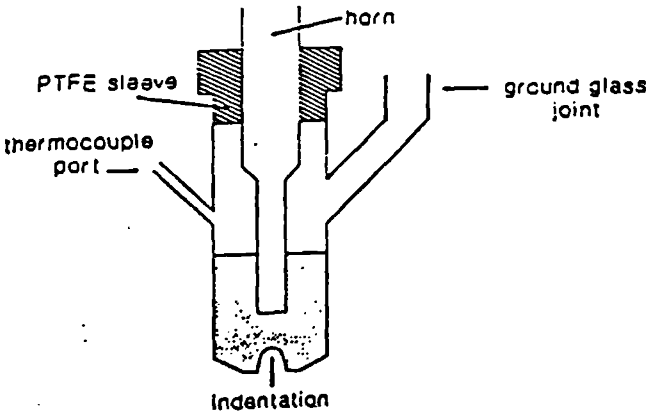
1.6.5 LABORATORY REACTION VESSELS

Work with sonic probes often involves the use of specially designed glassware. The Rosett cell consists of a glass flanged lid with loops at the base of the vessel. These loops are designed to aid mixing and cooling of the reaction mixture. However the loops may become blocked during heterogeneous reactions and therefore their efficiency is reduced. The probe is passed through a fitted PTFE sleeve, designed to seal the cell, into the vessel.

ROSETT CELL



DIMPLE CELL



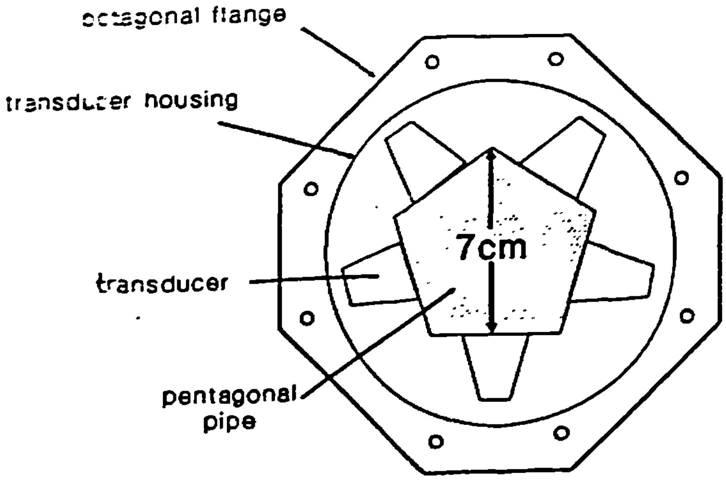
Other reaction vessels include glass vessels with indentations in the base (Dimple cells). These disperse sonic waves efficiently throughout the vessel due to the effect of ultrasonic streaming from the horn hitting the indent.

1.6.6 LARGE SCALE REACTORS

TUBE REACTOR

The tube reactor was developed with a view to large scale plant use. It consists of a stainless steel tube of pentagonal cross section and of varying length. Transducers are placed radially along the tube walls in a series of 3-2-3-2-2 giving a total of 12 transducers. This arrangement would mean that the highest intensity of ultrasound is found towards the centre of the tube. The reaction mixture passes through the pipe where it is sonicated. The design means it can be easily fitted to existing pipework and with the beam of sonic waves being focused into the centre of the pipe erosion is minimised.

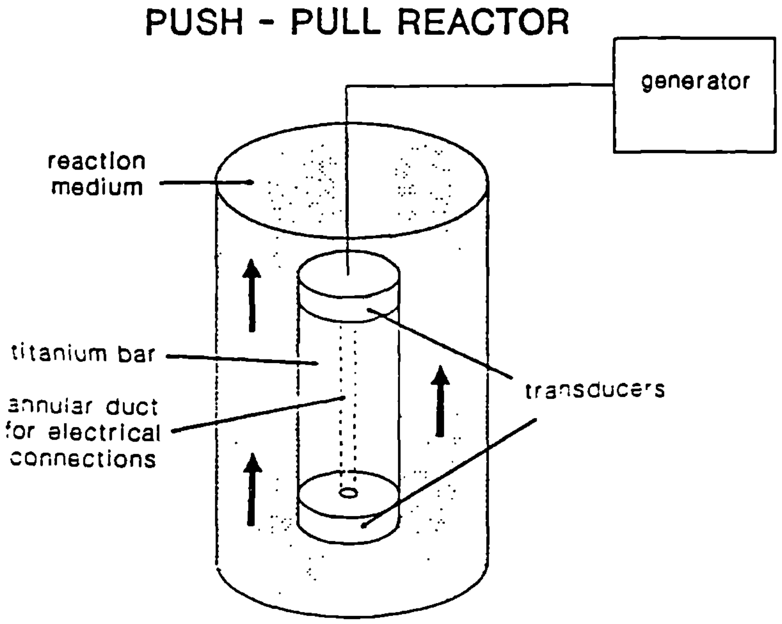
TUBE REACTOR



PUSH - PULL REACTOR

The Push - Pull equipment consists of a vertically mounted cylinder of titanium metal with a 20kHz transducer fixed to each end. The piezoelectric transducers vibrate at ultrasonic frequencies in an ' in and out ' manner. As a result the cylinder emanates horizontal waves of ultrasound from its walls.

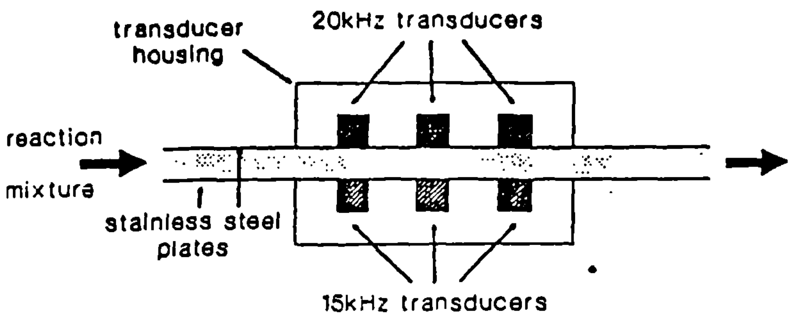
The Push - Pull machine is of variable power between 415 Watts and 1036 Watts and can be used either with its own reaction vessel or it can be placed alone in an existing bath or vat or passed through the centre of a tube.



NEARFIELD ACOUSTICAL PROCESSOR (NAP)

The NAP is a very powerful piece of ultrasonic equipment often used on the industrial scale. In this machine all the ultrasonic activity is "near field" . It operates by running the fluid to be processed between two narrowly spaced ultrasonic plates running slightly out of resonance with each other thus retaining the liquid in this intense ultrasonic field. A reverberatory system is created which is capable of providing a large amount of energy, approximately 800W, with an energy efficiency of 80%.

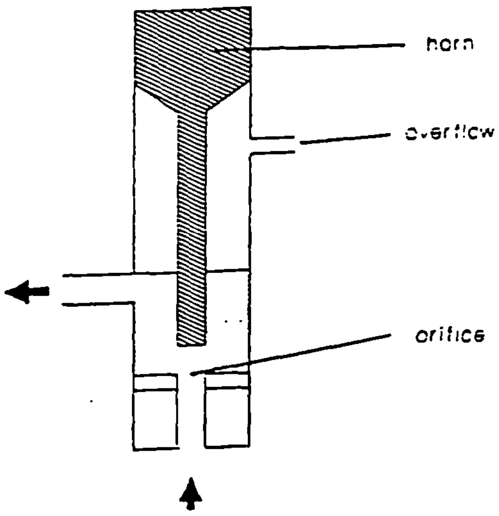
N.A.P SYSTEM



FLOW CELL

Flow cells are used for large scale reactions. They operate on a similar system to a whistle reactor in which a continuously flowing system is sonicated. In this case the sonication is provided via a probe. The flow cell is situated outside the main reaction vessel and the reaction mixture is sonicated as it passes through.

FLOW CELL



With better designed ultrasonic equipment becoming more available the application of ultrasound to organic synthesis is also becoming more widespread with a whole series of reactions being examined.

CHAPTER 2

EXPERIMENTAL

2.0 EXPERIMENTAL

This experimental section covers all the standard experiments upon which this thesis was based. More detailed information is given in the relevant chapters which follow.

This chapter is sub divided into ten sections which contain the following:-

2.1 - Details of the standard experiments employed for dosimetric and calorimetric analysis of the efficiency of sonochemical reactors. See chapter 3 for more details.

2.2 - Details of the sonochemical alkylation of 2,6-dimethylphenol upon which the effects of changes in fundamental parameters were investigated. Further details in chapter 4.

2.3 - Details of the sonochemical alkylation of 5-hydroxy-2-carboxylic acid ethyl ester with less reactive alkyl halides. See chapter 5 for further details.

2.4 - Details of the standard experiments employed for the dehydrogenation of Tetrahydonaphthalene. Further details in chapter 6.

2.5 - Details of the standard experiments employed to examine the effect of ultrasound on rice grains in an attempt to enhance rice gelation rate. See chapter 7 for further details.

2.6 - Details of the standard experiments employed to study the effect of ultrasound on the particle size reduction of sugar grains. See chapter 7 for further details.

2.7 - Details of the standard method for crystallisation rate enhancement by the application of sonication. Further details in Chapter 7.

2.8 - Details of the standard methods applied for examination of starch gelation, degradation and viscosity alterations. For further details see Chapter 8.

2.9 - Details of standard caramel preparations. See chapter 8 for more details.

2.10 - Details of the standard cocoa mixture preparation used in an effort to increase the amount of cocoa butter extracted from the cocoa grain. For further details see Chapter 8.

2.1 CHARACTERISATION OF ULTRASONIC EQUIPMENT

2.1.1 POTASSIUM IODIDE DOSIMETER

The 4% acidified potassium iodide solution employed in these experiments was prepared in the following manner. 4g of potassium iodide (Aldrich A.C.S Grade) was dissolved in a 100cm^3 of distilled water containing 1% 2M sulphuric acid. 10% carbon tetrachloride (Aldrich A.C.S Grade) was added to enhance the reaction.

For sonication with the sonic probe reaction vessels such as the dimple cell and Rosett cell, see earlier Chapter 1, were employed. The acidified potassium iodide and carbon tetrachloride solutions were added to the vessel and this in turn was placed into a water bath and the temperature within the vessel was monitored with a thermocouple. Addition of either ice or warm water to the water bath aided temperature control as sonication was applied. Samples were obtained after 30 seconds sonication and then at 1 minute intervals for a period of 5 minutes.

After sonication the sample was quickly removed and placed into an ice bath until it could be monitored by UV/Visible spectroscopy. All experiments and analyses were carried out as rapidly as possible to minimise the problem of air oxidation of the solution on standing.

A similar technique was applied when employing the sonic bath and stationary tube reactor, see earlier Chapter 1 for apparatus description. Temperature control is however difficult in these systems as addition of ice or establishing a flowing cooling system would result in disruption of the standing waves within the sonication area.

For flow systems samples were taken after every completed circuit of the solution through the reactor.

All results were analysed via UV/ Visible spectroscopy.

2.1.2 THERMAL REACTION CONDITIONS

100cm^3 of distilled was placed into a round bottomed flask and heated in a water bath to the required temperature. Once equilibrated 4g of potassium iodide and 10cm^3 of carbon tetrachloride were added and stirred for 2 hours at the required temperatures of 25°C, 35°C, 45°C, 55°C and 65°C. Samples were taken every 15 minutes initially then every 30 minutes. Results were analysed against distilled water using UV/ Visible spectroscopy.

2.1.3 FLOW SYSTEMS

Push-Pull Reactor

A flow system was also established employing the Push-Pull reactor, see earlier Chapter 1 for diagram of Push-Pull reactor. 6 Litres of acidified potassium iodide solution and 600cm^3 of carbon tetrachloride were pumped around the system at a constant flow of 100cm^3 of solution per 10 seconds. Circuit time for this system was 1 minute 40 seconds per 1 litre and approximately 10 minutes for 6600cm^3. The iodine yield was measured at the variable instrument settings of 415W, 503W, 600W, 700W, 801W and 901Watts power. The actual reactor has a sonication volume of 5 litres but 6.6 litres were processed.

Tube Reactor

A flow system was established employing a peristaltic pump a water reservoir and the tube reactor. 3600cm^3 of acidified potassium iodide solution and 360cm^3 of carbon tetrachloride were added to the tube reactor and pumped around the system at varying speeds utilising the peristaltic pump. Samples were taken during a period of 34 minutes after each completed circuit, note that circuit times varied with the flow rate for the solution of total volume 3960cm^3.

TUBE REACTOR FLOW TIMES		
PUMP SETTING	FLOW FOR 1 LITRE	FLOW FOR 4 LITRES
200	8 mins 30 secs	34 mins
300	5 mins	20 mins
400	3 mins 20 secs	13 mins 20 secs
500	2 mins 30 secs	10 mins
600	1 min 48 secs	7 mins 12 secs
700	1 min 40 secs	7 mins 4 secs
800	1 min 20 secs	5 mins 20 secs
900	1 min 10 secs	4 mins 41 secs

2.1.4 FRICKE DOSIMETER

The acidified ferrous ammonium sulphate solution employed for these experiments was prepared in the following manner. 0.98g of ferrous ammonium sulphate (Aldrich A.C.S Grade) was dissolved in 250cm^3 0.4M sulphuric acid.

The ferrous solution was added to the appropriate reaction vessel and placed into a water bath, for more effective temperature control, and sonicated with the sonic probe employing a 1.2cm diameter probe tip (setting 4, 10% output) for 60 minutes. Samples were taken at 5 minute intervals for the first 15 minutes and then at 15 minute intervals for 1 hour.

A similar technique was applied when employing the sonic bath and stationary tube reactor.

All experiments and analysis were performed immediately to avoid oxidation on standing

2.1.5 CALORIMETRY

Calorimetry can be used to measure the amount of ultrasonic power entering a reaction system by determining the temperature rise within the system in the first few moments of sonication. This is normally accomplished by monitoring the temperature rise of the solvent employing a thermocouple and taking readings every 5 seconds during the first minute of sonication. This change in temperature is then plotted against time and fitted to a polynomial equation. The first differential of the polynomial equation is equivalent to the rate of change of temperature with time. The rate of temperature change at time zero is obtained and this is multiplied by the solvent mass (or volume in the case of aqueous systems) and the specific heat capacity of the solvent. The amount of power, in watts, entering the system can thus be determined. Dividing the power entering the system by the area of the source of sonication or the total volume will give watts per square centimetre or watts per cubic centimetre respectively.

2.2 OPTIMISATION OF SONOCHEMICAL REACTION CONDITIONS

2.2.1 O-ALKYLATION OF PHENOLS AND ACETOPHENONES

The 'standard' O-alkylation reaction about which all further reactions were to be based is as follows:-

An initial reagent ratio of 1:2:2 of phenol: base: alkyl halide was employed.

100cm^3 of N-methylpyrrolidinone solvent was added to a dimple cell (see earlier Chapter 1). 5g (0.041 mols) of 2,6-dimethylphenol and 11.32g (0.082 mols) of potassium carbonate were also added and the cell placed into a preheated water bath at 45°C. When thermal equilibrium was established 13.96g (0.082 mols) of 1-iodopropane was added and the sample irradiated by sonic probe for 1.5 hours using a 1.2cm diameter tip. The 20kHz John Perkins sonic systems equipment was employed at a 15% output with 7.0 setting. The temperature within the cell was monitored with a thermocouple and kept at approximately 65°C. Aliquots of 0.5cm^3 were withdrawn half hourly and added to 1cm^3 of ethyl acetate and then neutralised with 1cm^3 of 2M sulphuric acid. All analysis was performed by GLC.

The corresponding thermal reaction employed the same conditions as above however the reaction cell was a round bottomed flask fitted with a condenser, thermometer and placed into a water bath at 65°C. Stirring was undertaken via a magnetic underwater stirrer. Work up of aliquots and analysis were performed as above.

2.2.2 Reaction with 1,3-dibromopropane

An initial reagent ratio of 2:1:1 of acetophenone: base: alkyl halide was employed.

100cm^3 of N-methylpyrrolidinone was added to a dimple cell. 4g (0.026 mols) of 2,6-dihydroxyacetophenone and 1.8g (0.013 mols) of potassium carbonate were also added and the cell placed into a preheated water bath at 45°C. When thermal equilibrium was established 2.62g (0.013 mols) of 1,3-dibromopropane was added and the sample was irradiated by sonic probe for 5 hours employing a 1.2cm probe tip. The 20kHz Sonics and Materials equipment was employed at a 32% output with 6 setting. The temperature within the cell was monitored with a thermocouple and kept at approximately 65°C. Aliquots of 0.5cm^3 were withdrawn half hourly and added to 5cm^3 of N-methylpyrrolidinone and the potassium carbonate was dissolved by the addition of a few drops of water, less than 1% total aliquot volume. All analysis was performed by HPLC.

The thermal reaction employed the same reagents as above however the reaction vessel was replaced by a 3 necked round bottomed flask fitted with a condenser, thermometer and magnetic follower. The round bottomed flask was placed into a preheated water bath at 65°c.

All treatment of aliquots and sample analysis was performed as for the sonicated reaction.

2.2.3 Reaction with Epichlorohydrin

100cm^3 of 4-methylpentan-2-one solvent was added to a dimple cell. 5g (0.033 mols) of 2,6-dihydroxyacetophenone and 2.27g (0.016 mols) of potassium carbonate were also added and the cell placed into a preheated oil bath set at approximately 120°C. When thermal equilibrium was established 1.52g (0.016 mols) of epichlorohydrin was added and the sample was irradiated by sonic probe for 5 hours employing a 1.2cm probe tip. The 20kHz Sonics and Materials equipment was employed at a 34% output with 8 setting. The temperature within the cell was monitored with a thermocouple and kept at approximately

130°C. Aliquots of $0.5cm^3$ were withdrawn half hourly and added to $5cm^3$ of N-methylpyrrolidinone and the potassium carbonate was dissolved by the addition of a few drops of water, less than 1% total aliquot volume. All analysis was performed by HPLC.

The reaction was also performed with N-methylpyrollidinone and dimethylformamide solvents.

The thermal reaction employed the same reagents as above however the reaction vessel was replaced by a 3 necked round bottomed flask fitted with a condenser, thermometer and magnetic follower. The round bottomed flask was placed into an electromantle and heated to 130°C. All treatment of aliquots and sample analysis was performed as for the sonicated reaction.

2.3 O-ALKYLATION OF 5-HYDROXYCHROMONE-2-CARBOXYLIC ACID ETHYL ESTER

2.3.1 ALKYLATION WITH 1-BROMOBUTANE

An initial reagent ratio of 1:2:2 of 5-hydroxychromone-2-carboxylic acid ethyl ester: base: alkyl halide was employed.

100cm^3 of N-methylpyrrolidinone was added to a dimple cell. 5g (0.02 mols) of 5-hydroxychromone-2-carboxylic acid ethyl ester was added with 5.8g (0.04 mols) of potassium carbonate. The cell was placed into a water bath and heated to approximately 45°C, the solvent temperature was monitored with a thermocouple. On reaching the required temperature 5.76g (0.04 mols) of 1-bromobutane was added. Probe sonication was applied via a 1.2cm diameter tip horn at 24% output (setting 6) with Sonics and Materials equipment. The temperature within the reaction vessel was monitored and kept at approximately 65°C. Aliquots 0.5 cm^3 were removed and added to 10cm^3 of N-methylpyrrolidinone containing 1% distilled water, to aid solubilisation of the base. The reaction was sonicated for 5 hours after which the reaction mixture was thrown into cold water and the precipitated solid filtered out. Sample analysis by HPLC and solid analysis by GLC/ Mass spectroscopy.

The corresponding thermal reaction was treated as above. The reaction vessel was a three necked round bottomed flask fitted with condenser, thermometer and underwater stirrer. Water bath temperature 65°C.

Both reactions were repeated with 2-bromobutane, 1-iodopropane and 2-bromopropane.

2.4 DEHYDROGENATION OF TETRAHYDRONAPHTHALENE

2.4.1 STANDARD REACTION CONDITIONS

25cm^3 of diethyleneglycol (digol) was added to a dimple cell. The cell was placed into an electromantle and heated to approximately 150°C, the solvent temperature was monitored with a thermocouple. On reaching the required temperature 3g (0.023 mols) of tetrahydronaphthalene was added with 0.1g of 3% activated charcoal/ palladium catalyst. Probe sonication was applied via a 0.3cm diameter tip horn at 17% output (setting 2) with the Sonics and Materials ultrasonic equipment. The temperature within the reaction vessel was monitored and kept at approximately 160°C. The reaction was sonicated for 6 hours and aliquots withdrawn hourly and filtered through silica to remove the solid catalyst. Samples were analysed by GLC.

The corresponding thermal reaction was treated as above but the solvent temperature was taken to 160°C. The reaction vessel was a three necked round bottomed flask fitted with a condenser, thermometer, nitrogen inlet and stirred with an overhead mechanical stirrer.

Thermal reactions were repeated at 180°C and 200°C whilst the sonicated reaction at 200°C was thought to be unnecessary as sonication already showed significant rate enhancement at the lower temperatures.

2.5 EFFECT OF ULTRASOUND ON RICE GRAINS

The standard rice mixture employed for these experiments is as follows: 50g of Sainsbury's White American Long Grain Rice or 50g of Sainsbury's Brown Rice added to 100cm^3 distilled water.

2.5.1 Thermal Reaction Conditions

The white rice was placed into a beaker to which water at varying temperatures, 60°C, 70°C, 80°C and Boiling, was added and maintained at these temperatures. The time taken for the white rice to gel was then recorded. Gelation was taken to be the point at which the white rice did not sink below the surface of the water on stirring.

From this procedure it was determined that white rice will not gel thermally below the temperature range of 75°C to 80°C. At 80°C it requires 15 minutes for white rice to gel and 25 minutes for brown rice.

2.5.2 Sonicated Reaction Conditions

2.5.2.1 Sonic Probe

The white rice was sonicated at 25°C, employing the Sonics and Materials equipment at setting 8 and output 32%, to determine if gelation would occur at this low temperature. It did not and therefore experiments were performed at elevated temperatures. Sonication was not attempted at 80°C with the sonic probe because it was considered that cavitation at temperatures nearing solvent boiling point would not be effective, although sonication at 80°C with both sonic bath and tube reactor was attempted. It was thought best to pre-sonicate the white rice, at room temperature, for a small period of time and then raise the temperature to 80°C and complete the gelation of the white rice thermally.

The white rice mixture was sonicated for periods of 1, 5, and 10 minutes at probe settings 2, 4, 6 and 8 on the Sonic and Materials Machine. The initial temperature was approximately 19°C and this temperature rose with sonication to approximately 30°C after 1 minute sonication, 50°C after 5 minutes sonication and over 60°C for 10 minutes, depending upon the power applied.

After pre-sonication the white rice mixture was placed into a water bath set to 80°C and the time to gel recorded. 80°C was reached after approximately 15 minutes in the water bath.

Brown rice was treated in a similar manner.

2.5.2.2 Sonic Bath

The white rice mixture was sonicated at 25°C for 10 minutes and then placed into a 80°C water bath and the gelation time was recorded. Gelation occurred after 30 minutes, this was the same result as was obtained for the conventional thermal reaction with untreated rice, *i.e.* 15 minutes to reach 80°C and 15 minutes to gel at this temperature.

White rice mixture at 25°C was added to a sonic bath containing 80°C water and sonicated until gelation occurred. Gelation occurred as for the conventional thermal reaction. There was no improvement over conventional thermal methods.

Water at 25°C was placed into a small sonic bath. The brown rice was sonicated for 10 minutes and then added to an 80°C water bath. Once 80°C was attained the brown rice gelled within 19 minutes, this represented a 25% reduction in gelation time over conventional thermal methods where gelation occurred after 25 minutes at 80°C.

2.5.2.3 Tube reactor

The white rice/water mixture was added to a glass vessel and sonicated for 10 minutes at 25°C in the tube reactor. The temperature rose to approximately 45-50°C. The white rice was then placed into the 80°C water bath and the gelation time was recorded. The gelation time was again similar to conventional thermal results with no improvement.

White rice at 25°C was placed into a tube and added to the tube reactor containing water at 80°C and sonicated until gelation occurred. There was no improvement over conventional thermal gelation.

The white rice mixture was added directly to the tube reactor at 25°C. The mixture was stirred and sonicated. A sample of white rice was withdrawn after 10 minutes and added to an 80°C water bath. Gelation occurred after 31 minutes with no improvement over thermal reaction conditions. Sonication was continued. 80°C was reached in the tube reactor after 19 minutes sonication and boiling point was reached after 38 minutes. At this time not all the water had been absorbed and sonication was discontinued as there was no improvement over thermal conditions.

2.5.3 THE EFFECT OF ULTRASOUND ON STARCH EXTRACTION

White and brown rice grains were washed thoroughly to remove any surface starch and dried in an oven overnight. 50g of white rice was weighed accurately, added to 100cm^3 of distilled water and sonicated for 5 minutes employing the Sonics and Materials equipment with a 1.2cm probe tip at setting 8 with 32% output. The surfactant water was carefully removed and filtered through a sintered funnel of porosity No3 with a second paper filter, of a similar porosity, placed over the funnel to enable efficient collection of starch. To remove all starch released during the experiment the rice was washed with a further 500cm^3 of distilled water which was again carefully filtered. The remaining rice was dried in an oven, at 65°C, as was the filter paper containing starch. The total mass of starch released from the rice grains was calculated. The experiment was repeated employing brown rice grains.

As a controlled experiment 50g of white rice grains was added to 100cm^3 of distilled water and the mixture was vigorously stirred for 5 minutes. After stirring the mixture was filtered and treated as above.

2.5.4 MICROWAVE CONDITIONS

50g white rice was added to 100cm^3 of distilled water at an initial temperature of 17.9°C and placed into a 700W domestic microwave oven (model number Proline M3030). The temperature of the white rice/water mixture at the bottom at the beaker was assumed to be the temperature within the white rice granules. This temperature was found to lag behind that of the supernatant water. The results are as follows:-

10 sec - temp 26.2°C

30 sec - temp 34.2°C

60 sec - temp 60.6°C

90 sec - temp 87.0°C

120 sec - temp 92.9°C

150 sec - temp 96.0°C water boiling

After 300 seconds there is no water left and the white rice remains uncooked. In an attempt to eliminate this problem more water was added thus 50g of white rice was added to 200cm^3 of distilled water.

After 120 seconds the temperature within the white rice rose to 82.3°C and after 300 seconds the water was boiling fiercely. 7 minutes microwave application resulted in less water present but the white rice remained uncooked and the water level decreased further after 8 minutes microwave application. After 9 minutes there was a slight amount of water remaining and the white rice appeared to be more or less cooked although individual white rice grains were distinctly visible. 10 minutes microwave application resulted in totally cooked white rice which appeared to have a 'fluffy' appearance with individual grains visible and no gelation, unlike the conventional thermal method. Any further application of microwaves would have resulted in the white rice becoming burnt as there was no water remaining at this stage.

2.5.5 THE EFFECT OF SONICATION ON THE GELATION OF GROUND RICE

2.5.5.1 Thermal reaction conditions

25g of ground rice was added to 100cm^3 of distilled water. This mixture was placed into an 80°C water bath and the temperature and time of gelation was noted. 50°C was reached in 2.5 minutes and 60°C in 4 minutes. The rice mixture began to thicken as 68.0°C was reached. After 6.5 minutes 70°C was attained and maximum density was achieved. A very granular gel was obtained.

2.5.5.2 Sonicated reaction conditions

Sonic probe

A similar mixture of ground rice and water was sonicated, employing the Sonics and Materials equipment with a 1.2cm probe tip at setting 8 with 32% output, and the temperature allowed to rise. The solution thickened after 9 minutes as 67°C was reached and sonication was no longer possible after 10 minutes 20 seconds. A dense lumpy mixture was obtained which was less granular than the gel obtained thermally. This suggested that the size of the rice granules must have been reduced on sonication. The rice mixture was therefore pre-sonicated in an ice bath for 10 minutes and then the temperature was raised in order to determine gelation time. A lumpy gel with a smaller grain size was obtained after 6.5 minutes as 70°C was attained.

Sonication does not reduce the time or the temperature of ground rice gelation. It does however appear to reduce the grain size.

2.6 THE EFFECT OF ULTRASOUND ON SUGAR GRAIN SIZE

2.6.1 Sonic Probe

50cm^3 of solvent, either vegetable oil or dimethylformamide, was added to 12.5g of granulated, or icing, sugar and sonicated, employing the Sonics and Materials equipment, with a 20kHz 1.2cm diameter probe tip for 30 minutes, setting 6 at 14% output. Small samples of sugar were withdrawn and placed into a cuvette containing a magnetic stirrer and dimethylformamide. The cuvette was placed into the Galai particle size machine and the stirrer was activated. Information was collected and the average particle size determined.

2.6.2 Tube Reactor

1000cm^3 of vegetable oil was added directly to the tube reactor and 250g of granulated sugar added. Stirring was attempted with an overhead stirrer but this proved to be ineffective. Sugar settled to the base of the tube reactor and subsequent analysis of the particles indicated no size reduction.

170cm^3 of solvent, either dimethylformamide or vegetable oil, was added to a 26.5mm diameter glass vessel. 42.5g of granulated sugar was added to the vessel which was placed into the tube reactor, containing water at 25^{o}C, and sonication was commenced. Samples were withdrawn and added to a cuvette containing dimethylformamide and magnetic stirrer. The cuvette was placed into the Galai particle size machine and the stirrer activated, information collected and average particle size determined. Sugar settled to the base of the reaction vessel and subsequent analysis of the particles indicated no size reduction. When icing sugar was employed some particle size reduction was observed.

2.7 THE EFFECT OF ULTRASOUND ON SUGAR CRYSTALLISATION

Sugar solutions were prepared by adding the required sugar compositions to the required amount of water and heating this mixture until clarity was reached and no undissolved sugar granules were observed. Some of the non-sonicated samples were then seeded, others were not. Sonicated samples were seeded and sonicated for the required time, usually 10 seconds, before analysis.

2.8 THE EFFECT OF ULTRASOUND ON STARCH

The cornflour mixture employed in all the experiments was prepared as follows:

30g of the required cornflour type; either cornstarch, amylose, amylopectin or soluble starch, were added to $100cm^3$ of distilled water.

Custard was prepared in a slightly different manner. 20g of custard powder and 5g of dried milk powder was added to $100cm^3$ of distilled water.

2.8.1 STARCH GELATION

2.8.1.1 Thermal Reaction

$100cm^3$ of water was heated to the required temperature and added to 30g of starch or 25g custard mixture. The temperature was kept constant and stirring applied until gelation occurred.

2.8.1.2 Sonic Probe

The Sonics and Materials equipment was employed with a 1.2cm probe tip at various settings from 2 to 8. 30g of starch/ 25g custard mixture was added to $100cm^3$ of distilled water. Sonication was applied and proved to be an efficient method for powder dispersion, external stirring was not required at high powers. Initially the temperature of the experiment was kept at 25°C but when no improvement in gelation was observed the reaction temperature was allowed to rise with application of sonication and the effect on gelation was monitored.

2.8.1.3 Sonic Bath

In the case of custard gelation the sonic bath was also employed as a source of ultrasound. 25g of custard mixture was added to 25°C distilled water contained in a conical flask. The temperature of the mixture was allowed to rise. Due to the low power of the bath powder dispersion was poor and external stirring, or pre-mixing of the mixture was necessary to avoid irregular sonication and heating and therefore uneven gelation.

The coupling medium within the sonic bath, detergent plus water, was heated to 80°C and the pre-mixed custard was added to the conical flask. The mixture reached 71°C within 30 seconds of sonication indicating good heat transfer from the surrounding medium.

2.8.1.4 Tube Reactor

Sonication of the custard mixture was attempted employing the tube reactor with and without the 26.5mm diameter glass vessel. Water at 80°C was added to the tube reactor to act as the coupling medium when the glass vessel was employed. 35g of custard powder and 8g of milk powder was added to 170cm^3 of 25°C distilled water in the glass vessel and placed into the tube reactor. On sonication however the powders were not efficiently dispersed and floated to the surface of the vessel. Pre-mixing before addition to the glass vessel was necessary. On sonication 70°C was reached after only 2 minutes 5 seconds indicating a very efficient heat transfer between the surrounding medium and the bulk solution.

In the absence of the glass vessel the whole of the tube reactor was employed as the reaction vessel. This involved the use of 300g of custard powder and 60g of dried milk powder added to 1500cm^3 of 25°C distilled water. The custard was pre-mixed before addition to the tube reactor and the temperature within the tube was allowed to rise as sonication was applied. 70.0°C was reached after 48 minutes 15 seconds sonication and gelation complete at 74.5°C between approximately 52 minutes 45 seconds and 53 minutes 45 seconds.

2.8.1.5 Microwave Conditions

20g of custard and 5g of milk powder was added to 100cm^3 of distilled water and subjecting to 700W microwave irradiation. Inefficiency in heat distribution occurred with the surface retaining heat more efficiently than the bulk solution, and thus mixing was required to ensure efficient heat distribution and a more uniform gel. Irradiation was therefore applied in 10 second bursts to allow for stirring. 70°C was reached after 70 seconds and coincided with the onset of gelation.

2.8.2 STARCH DEGRADATION

2.8.2.1 Degradation of Concentrated Starch

30g of starch powder was added to 30cm^3 of distilled water. This mixture was gelled by the application of sonication and also by allowing the solution temperature to rise.

Sonication was applied via 1.2cm probe tip utilising the Sonics and Materials equipment, setting 8 with 33% output. A solid paste was obtained and a further 70cm^3 of water was added. The temperature was raised to approximately 70 - 75°C. Gelation occurred at 70°C indicating no large degree of degradation of the starch molecules.

A similar thermal experiment was attempted. The starch was initially gelled thermally to give the concentrated paste and again re-gelled thermally after the second addition of water. As expected the cornflour paste did not appear to degrade thermally.

2.8.2.2 Degradation of Gelled Starch

30g of starch powder was added to 100cm^3 of water. Gelation was completed via thermal methods. A gel in which the inter/intramolecular forces are not as strong as in the concentrated sample was obtained. In an effort to reduce the viscosity of the sample sonication was applied via 1.2cm probe tip employing the Sonics and Materials equipment, setting 8 at 30% power output. Within 5 minutes a reduction in viscosity was observed, in the case of amylopectin this was a permanent effect. For amylose the reduction was temporary but surprisingly in the case of cornstarch, which is a mixture of amylopectin and amylose, there was no reduction in viscosity at all. Alterations in viscosity were clear enough to be judged by the naked eye.

2.9 EFFECT OF SONICATION ON CARAMEL

2.9.1 3:1 TOTAL SUGAR/ TOTAL WATER RATIO

RECIPE EMPLOYED

For a 500g batch:

	%	Moisture	Mass
Skimmed Milk	9.5%	-	47.5g
Sugar	17.9%	-	89.5g
Water	14.0%	14.0%	70.0g
Glucose Syrup	42.3%	7.8%	211.5g
Fat	15.6%	-	78.0g

In the Presence of Water

2.9.1.1 Thermal Preparation

To 55cm^3 of water 47.5g of milk powder was added and this mixture was stirred for 10 minutes at 300rpm. 89.5g of granulated sugar was added and stirring was continued for a further 5 minutes whereupon 78g of hardened vegetable fat was added together with 15cm^3 of water and 211.5g of glucose syrup. This mixture was then heated for approximately 15 to 20 minutes until a temperature of 113°C was obtained. The caramel was then removed from the heat and left to cool overnight.

2.9.1.2 Initial Low Power Sonication then Thermal Completion

55cm^3 of water and 47.5g of milk powder were added directly to a small sonic bath. The mixture was then sonicated for 5 minutes after which 89.5g of granulated sugar was added and sonication continued for a further 5 minutes. The fat was subsequently added and sonication continued for a final 5 minutes. The temperature within the small sonic bath reached 45°C. This mass was then transferred to the glucose syrup and extra water mixture on a heating mantle and heated and stirred, at 300rpm, until 113°C was reached. The glucose syrup and the fat were quite solid and the mass had to be heated for a few minutes before the stirrers could be induced to move.

On reaching 113°C the caramel was removed from the heat, poured onto waxed paper and left overnight to cool.

2.9.1.3 In the Absence of Added Water

In this case all the water additions had been omitted. 113°C was reached very quickly, as there was no water to remove from the system and the thermal capacity of a viscous liquid is much greater than the standard caramel mix, thus the caramel had to be removed from the heat before complete browning had occurred resulting in a pale caramel.

2.9.1.4 Full Low Power Sonicated Preparation

The glucose syrup and fat were both melted and this mixture was then transferred into the small sonic bath whereupon the milk and granulated sugar were added. The powders were mixed into the oil with gentle stirring and sonication was applied for 45 minutes. The temperature within the bulk of the caramel was monitored, see below. Browning began after 20 minutes sonication in the centre of the bath with the caramel temperature at approximately 87°C. The mixture was stirred occasionally to assist with the distribution of solids throughout the mixture.

Temperatures reached in the sonicated caramel:-

20 minutes - 87°C

25 minutes - 97°C

30 minutes - 103°C

35 minutes - 103°C

40 minutes - 103°C

The temperature of the caramel within the sonic bath did not rise above 103°C. The browning reaction of the caramel occurred due to the long residence time of the caramel within the sonic bath and the slow heating of the caramel during sonication.

Sonication was discontinued after 45 minutes in the sonic bath and the caramel mixture was separated into two halves. One half of the caramel was transferred directly to waxed paper and left to cool. The second half of the caramel was transferred from the bath and thermally heated to 113°C, with stirring at 300rpm in order to complete the preparation. After the required temperature had been reached the caramel was poured onto waxed paper and left overnight to cool.

2.9.2 5:1 TOTAL SUGAR/ TOTAL WATER RATIO

A series of further experiments were performed with a lower moisture content caramel.

RECIPE EMPLOYED

For a 500g batch:

	%	Moisture	Mass
Skimmed Milk	11.0%	-	55.0g
Sugar	20.9%	-	104.0g
Water	8.9%	8.9%	45.0g
Glucose Syrup	61.1%	11.3%	306.0g
Fat	18.2%	-	91.0g

In the Presence of Water

2.9.2.1 Addition of Milk Powder to Sucrose

Here the order of addition was altered. 104g of sugar was added to 45 cm^3 of water and the mixture was stirred until all the sugar had dissolved. 55g of milk powder was then added and the mixture was stirred for 15 minutes at 300rpm. The milk, sugar and water formed solid granules. At this point 91g of melted fat and 306g of melted glucose syrup were added and the whole mixture was stirred and heated to 113°C. It was then poured onto wax paper and left to cool and stand overnight.

2.9.2.2 Higher Power Sonication and then Thermal Completion

The experimental procedure of this experiment was as for the low powered experiment however the sonication of the sugar and water mixture was provided by a higher powered sonic probe, from the Sonics and Materials equipment, for only 5 minutes at setting 8, 40% power output.

2.9.3 ADDITION OF MILK POWDER TO GLUCOSE SYRUP

In these sets of experiments milk powder was mixed directly with glucose syrup and stirred/ sonicated for 15 minutes after which the remaining ingredients were added.

RECIPE EMPLOYED

For a 500g batch:

	%	Moisture	Mass
Skimmed Milk	11.0%	-	55.0g
Sugar	20.9%	-	104.0g
Water	8.9%	8.9%	45.0g
Glucose Syrup	61.1%	11.3%	306.0g
Fat	18.2%	-	91.0g

2.9.3.1 Thermal Preparation

306g of glucose syrup was melted and 45cm^3 of water and 55g of milk powder were added to it. This mixture was stirred for 15 minutes, at 300rpm, after which the 104g of sugar and 91g of fat were added. The mixture was then heated to 113^{o}C and left to cool and stand overnight.

2.9.4 7:1 TOTAL SUGAR/ TOTAL WATER RATIO

A batch of low water content caramel was prepared and heated mainly by the heat produced due to sonication by either the small sonic bath or the sonic probe.

RECIPE EMPLOYED

For a 500g batch:

	%	Moisture	Mass
Skimmed Milk	9.7%	-	48.5g
Sugar	18.3%	-	91.5g
Water	7.8%	7.8%	39.0g
Glucose Syrup	48.4%	4.8%	242.0g
Fat	15.9%	-	79.0g

Note in this recipe the glucose syrup was first heated to 120°C to produce a 90% solids syrup before it can be used in any preparation.

2.10 EFFECT OF ULTRASOUND ON DISPERSIONS

2.10.1 INTRODUCTION

The initial experimental idea for this exercise was to investigate the possibility that ultrasound might be able to release more cocoa butter from cocoa than conventional technology.

Cocoa grains contain 55% of cocoa butter however in the production of chocolate more cocoa butter must be added. Cocoa butter is a valuable commodity used extensively in foods but also in beauty preparations such as moisturisers. Cocoa butter is removed from cocoa beans by extrusion, this process generally leaves approximately 12% of the butter in the residue which is discarded. This is a considerable waste of a valuable product. It was thought that disruption of the cocoa grain under sonication would occur and thus allow a more efficient extraction of its cocoa butter reducing the overall loss of this material.

The cocoa mixture used for experimentation was prepared as follows:

5g of cocoa powder was added to 100cm^3 of water. In cold water most of the cocoa floats on the surface and becomes very difficult to 'wet'. The cocoa powder agglomerates into lumps with wet cocoa powder surrounding an internal core of dry cocoa. The cocoa mixture had to be prepared with hot water which separates the grains, coats them efficiently and allows them to sink. It is this hot water cocoa, when cooled to room temperature, which was employed in all the following experiments.

CHAPTER 3

CHARACTERISATION OF ULTRASONIC EQUIPMENT

3.0 CHARACTERISATION OF ULTRASONIC EQUIPMENT

3.1 INTRODUCTION TO CHEMICAL DOSIMETRY

Dosimetry is a method of calibrating ultrasonic equipment with respect to the effect of power output (or intensity) on a chemical reaction. It can be used as a method of comparing the efficiency of ultrasonic equipment, determining the optimum dimensions of reaction vessels (*i.e.* sonochemical reactors) and also as a method of determining the best match for reaction volume with ultrasonic power used.

Suslick et al[30] utilised three dosimeters to evaluate the efficiency of sonication for several pieces of equipment. The oxidation of iodide ion to iodine in aqueous potassium iodide solution is well known. It relies on the formation of hydrogen peroxide from the homolytic fission of water under sonicated conditions to produce the source for the iodide oxidation. Sonication results in an oxidation rate some 4 magnitudes greater than that obtained via normal air oxidation.

Diphenylpicrylhydrazyl (DPPH) is a stable free radical often employed as a radical trapping agent. Its intense blue colour may be easily monitored and as a dosimeter the bleaching of DPPH is useful in non-aqueous solutions and enables radical formation due to sonolysis to be observed.

Finally the ironpentacarbonyl $Fe(CO)_5$ dosimeter may be employed. Under thermal conditions $Fe(CO)_5$ forms iron metal and carbon monoxide. Under photolytic conditions $Fe(CO)_4$ is initially formed and this reacts with $Fe(CO)_5$ to form the dimer $Fe_2(CO)_9$. However sonication produces a different result yielding finely divided iron and the trimer $Fe_3(CO)_{12}$. These materials are not formed thermally or photolytically and there is no evidence of the $Fe_2(CO)_9$ dimer in the sonochemical reaction. The rate of formation of

$Fe_3(CO)_{12}$ trimer is taken as an indication of the sonochemical efficiency.

3.1.1 Sonolysis Reactions of Aqueous and Non-Aqueous Solvents

Weissler[31] attempted to explain radical formation in sonicated aqueous solutions by examining the production of hydrogen peroxide. By monitoring the hydrogen peroxide levels in the presence of radical scavengers it was noted that the rate of hydrogen peroxide production fell as the levels of scavengers were increased. This suggested that hydrogen peroxide was formed via a radical reaction.

Weissler also stated that in radiation chemistry, in oxygenated solutions, hydrogen peroxide may be formed by the following reaction via the hydroperoxy radical. In this way hydrogen peroxide could also be formed via radical reaction with oxygen and not exclusively via radical recombination.

$$H^{\cdot} + O_2 \rightarrow HO_2^{\cdot}$$

$$2HO_2^{\cdot} \rightarrow H_2O_2 + O_2$$

Hart and Henglein[32] noted that the rate of hydrogen peroxide production in an argon atmosphere could be increased to a maximum point as oxygen levels were increased. This was thought to be due to radical reaction with the atmospheric oxygen within the cavitation bubble via several steps.

$$H_2O \rightarrow H^{\cdot} + OH^{\cdot}$$

$$H^{\cdot} + O_2 \rightarrow HO_2^{\cdot}$$

$$HO_2\cdot + H\cdot \rightarrow H_2O_2$$

$$HO_2\cdot \rightarrow H_2O_2 + O_2$$

$$HO_2\cdot \rightarrow OH\cdot + O\cdot$$

$$O\cdot + H_2O \rightarrow 2OH\cdot$$

$$2OH\cdot \rightarrow H_2O_2$$

Riesz et al[33] investigated the three possible regions in which sonochemical radical reactions could occur:

a) In the cavitation bubble itself where very high temperatures and pressures result in the homolytic fission of aqueous volatile solutes to give free radicals.

b) At the bubble interphase at intermediate temperatures where the products are similar to those obtained in pyrolysis reactions with non-volatile solutes.

c) The third region is the low temperature bulk solution where the radicals produced in the cavitation bubble or at the interphase escape and undergo scavenging reactions with solutes and to produce products similar to those seen in aqueous radiation chemistry.

Volatile solutes under sonication conditions would be expected to be found in the cavitation bubble itself as would traces of the soluble gas from the atmosphere. The dissociation of water to hydrogen and hydroxyl radicals is thought to occur initially in the cavitation bubble. The sonolysis of aqueous solutions of volatile alcohols such as methanol and ethanol produce methyl radicals, via decomposition of the alcohols within the cavitation bubble. The radicals then diffuse into the bulk solution where they can be spin trapped and identified by ESR.

The sonolysis of dilute solutions of non-volatile solutes such as acetates, amino acids and sugars result in the formation of radicals through typical hydrogen and hydroxyl radical addition or abstraction reactions. At higher concentrations other radicals can be identified such as methyl radicals, thought to be formed via pyrolysis reactions at the bubble interphase.

Suslick et al[16] demonstrated that the sonolysis of alkanes produced a variety of low molecular weight alkanes and alkenes. They postulated that C-C bond cleavage can occur and radical elimination or hydrogen abstraction from the solvent then leads to the formation of H_2, CH_4, C_2H_2 and other small hydrocarbons similar to those obtained during high temperature pyrolysis or shock tube treatments.

Isotope exchange reactions between hydrogen and deuterium in a liquid can be induced by sonolysis and are thought to be due to multiple radical reactions within the cavitation bubble. Fischer at al[15] examined the exchange of hydrogen with deuterium during the sonolysis of water in an argon/ deuterium atmosphere. Sonolysis of water produces hydrogen and hydrogen peroxide via radical combination reactions and in the presence of an oxygen atmosphere the yields of some decomposition products may be enhanced. For example under an argon/ deuterium atmosphere yields of H_2 (and HD) are much higher than the yields of H_2 (and H_2O_2) observed under pure argon in the absence of deuterium. This is thought to be due to the effect of deuterium on the recombination reaction of $H^\cdot$ and $OH^\cdot$ radicals.

$$H^\cdot + OH^\cdot \rightarrow H_2O$$

At low concentrations of deuterium mainly hydroxyl radicals are scavenged to form HOD and the hydrogen radicals go on to form H_2 and/ or HD. At higher concentrations of deuterium hydrogen also becomes scavenged through the reaction:-

$$H^{\cdot} + D_2 \rightarrow HD + D^{\cdot}$$

This results in the formation of more HD than H_2.

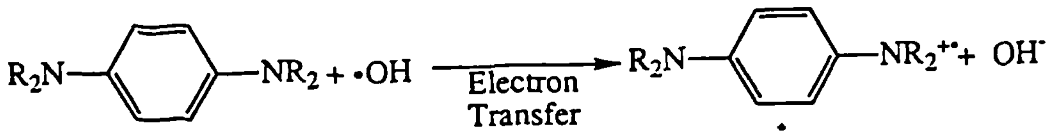
The dissociation of deuterium to deuterium radicals in the cavitation bubble has been ruled out since the levels of HD produced are too low and the H_2 levels are too high for this step to be a major reaction route.

3.1.2 Evidence for radicals

Makino et al[34] obtained conclusive proof for the presence of $OH^{\cdot}$ and $H^{\cdot}$ radicals during the sonolysis of aqueous solutions. Employing non-volatile nitrone spin traps such as 5,5-dimethyl-1-pyrroline-1-oxide (DMPO) ESR spectra were obtained which displayed the characteristics expected for $OH^{\cdot}$ and $H^{\cdot}$ adducts of DMPO. To prove that $OH^{\cdot}$ and $H^{\cdot}$ radicals were formed via the sonolysis of water experiments were performed where radical scavengers competed with the spin traps for $OH^{\cdot}$ and $H^{\cdot}$ radicals. Addition of the radical scavenger sodium formate indicated that for a constant concentration of DMPO, as the radical scavenger concentration is increased the OH-DMPO radical adduct decreases indicating a competitive reaction occurring.

Zhang et al[35] reported the formation of a series of radical cations via the sonolysis of aqueous N-tetraalkyl-p-phenylenediamines. It is suggested that on sonolysis the aqueous solution forms $OH^{\cdot}$ radicals and via a single electron transfer the corresponding alkyl radical cation is produced. In this study both $OH^{\cdot}$ radical and the tetraalkyl-p-phenylenediamine radical were identified by ESR techniques.

$$H_2O \xrightarrow{\text{Sonolysis}} \cdot OH + \cdot H$$



Krishna et al[36] utilised spin-trapping techniques to determine the various products obtained from the sonolysis of aqueous solutions of ethanol, 1-propanol, 2-propanol and 2-methyl-2-propanol. The sodium salt of 3,5-dibromo-4-nitrosobenzenesulphonate was employed as the spin trapping agent. For this spin trap the sulphonate group ensures non-volatility and the radical adducts have well characterised spectra. The results are summarised below.

SOLVENT SYSTEM

	RADICALS PRODUCED
Argon saturated aqueous methanol	$CH_3\cdot$ and $\cdot CH_2OH$
Ethanol/ Water (5%)	$CH_3\cdot$, $CH_2\cdot$, $\cdot CH_2\text{-}CH{=}O$, $CH_3CH_2\cdot$
1-Propanol/ Water (1%)	$CH_3\cdot$, $CH_3C{\cdot}HCH_2OH$, $CH_3CH_2C{\cdot}HOH$, $\cdot CH_2CH_2CH_2OH$ plus 2 uncharacterised (2 adducts by photolysis)
2-Propanol/ Water (1%)	$CH_3\cdot$, $CH_3CHOHCH_2\cdot$, $\cdot CH_2COCH_3$ (1 adduct by photolysis)
2-Methyl-2-Propanol/ Water (1%)	$CH_3\cdot$, $\cdot CH_2(CH_3)_2\text{-}COH$, $(CH_3)_3C\cdot$

For these systems sonolysis appears to give different adducts to those obtained via photolysis or radiolysis.

Christman et al[37] obtained evidence for the production of free radicals in aqueous solutions due to microsecond pulsed ultrasound. Employing spin traps such as 5,5-dimethyl-1-pyrrolidine-N-oxide (DMPO) and α-4-pyridyl-1-oxide-N-tert-butylnitrone (4-POBN) the ESR spectra obtained provided evidence for the formation of the free radicals $OH^{\cdot}$ and $H^{\cdot}$.

Conclusive evidence for the generation of $OH^{\cdot}$ from the sonolysis of aqueous systems was obtained by the addition of ethanol to the solutions. Ethanol is a well known $OH^{\cdot}$ scavenger and any $OH^{\cdot}$ generated will react with ethanol to give the CH_3CHOH radical which will go on to form the ethanol spin adduct rather than the $OH^{\cdot}$ radical adduct. If the hydroxyl spin adduct is formed via a radical mechanism the addition of ethanol should prevent its formation, which was the result obtained.

3.1.3 THE SONOLYSIS OF ORGANIC SOLVENTS

Generation of radicals via the sonolysis of pure organic liquids was not thought possible until Weissler, Pecht and Anbar[38] examined the effects of sonicating pure acetonitrile and pure carbon tetrachloride.

The sonolysis of argon saturated acetonitrile resulted in the formation of nitrogen, hydrogen and methane. With oxygen present carbon monoxide, carbon dioxide and water were also formed indicating that the nature of the dissolved gas is of importance. The decomposition of pure carbon tetrachloride during sonolysis was monitored by the generation of chlorine gas. The amount could be increased by the addition of n-butyl iodide to the system which prevented the reaction of chlorine gas with $CCl_3^{\cdot}$ radicals.

Jennings and Townsend[39] investigated the sonolysis of carbon tetrachloride under an argon atmosphere. No decomposition products were observed until a small amount of water was added when chlorine, carbon dioxide, oxygen and the chlorinated hydrocarbons C_2Cl_6 and C_2Cl_4 were detected. This result led to the conclusion that a free radical mechanism must be present. Chlorine and C_2Cl_6 being formed via radical combination reactions.

$$CCl_4 \ \text{->}\ CCl_3\cdot + Cl\cdot$$

$$2Cl\cdot \ \text{->}\ Cl_2$$

$$2CCl_3\cdot \ \text{->}\ C_2Cl_6$$

The absence of Cl_2 from the sonolysis of pure $CHCl_3$ is thought to be due to the fact that the C-H bond is broken in the preference to the C-Cl bond to give the more stable $CCl_3\cdot$ radical.

$$CHCl_3 \ \text{->}\ H\cdot + CCl_3\cdot$$

rather than

$$CHCl_3 \ \text{->}\ Cl\cdot + CHCl_2\cdot$$

Any Cl· formed via the above reaction will probably react with a second molecule of $CHCl_3$ to give products via the low activation energy pathway as follows:-

$$Cl\cdot + CHCl_3 \ \text{->}\ HCl + CCl_3\cdot$$

resulting in no Cl· radical recombination reaction.

The free radical mechanisms proposed are as follows:-

The sonolysis of aqueous carbon tetrachloride is thought to proceed via the following pathway.

$$H\cdot + CCl_4 \rightarrow HCl + CCl_3\cdot$$

$$Cl\cdot + CCl_4 \rightarrow Cl_2 + CCl_3\cdot$$

$$HO\cdot + CCl_4 \rightarrow HOCl + CCl_3\cdot$$

Sonolysis of aqueous $CHCl_3$ produced oxygen and smaller amounts of the chlorinated hydrocarbons but no chlorine.

$$H\cdot + HCCl_3 \rightarrow H_2 + CCl_3\cdot$$

$$H\cdot + HCCl_3 \rightarrow Cl\cdot + HCCl_2\cdot \text{ less likely step}$$

$$Cl\cdot + HCCl_3 \rightarrow HCl + CCl_3\cdot$$

No hydrogen peroxide was detected during sonication of either CCl_4 or $CHCl_3$ in the presence of water. The reasons for this are thought to be different in each system.

In the case of carbon tetrachloride the sonochemically generated chlorine will react with the H_2O_2 as follows:-

$$Cl_2 + H_2O_2 \rightarrow 2HCl + O_2$$

This accounts for the steady state concentration of chlorine and also for the production of oxygen. If chlorine is formed at a faster rate than hydrogen peroxide then no hydrogen peroxide will be detected since the decomposition reaction will consume the hydrogen peroxide as fast as it is produced.

In the case of $CHCl_3$ the sonochemically generated $OH\cdot$ is likely to react with the solvent as follows:-

$$HO\cdot + HCCl_3 \rightarrow HOH + CCl_3\cdot$$

rather than to undergo dimerisation to produce hydrogen peroxide.

$$2HO\cdot \rightarrow H_2O_2$$

Rosenthal[40] investigated the sonolysis of carbon tetrachloride and trichlorobromomethane by ESR. The free radicals generated were identified by spin trapping with 2-methyl-2-nitrosopropane and evidence was obtained for the generation of $Cl\cdot$ in both systems under air and nitrogen atmospheres.

3.2 THE USE OF AQUEOUS POTASSIUM IODIDE AS A DOSIMETER FOR SONOCHEMISTRY

Weissler et al[41] stated that sonication of an aqueous solution of potassium iodide half saturated with carbon tetrachloride resulted in a five fold rate enhancement in the liberation of iodine when compared to that of potassium iodide solution in the absence of carbon tetrachloride. Keeping the potassium iodide solution fully saturated with carbon tetrachloride resulted in an over 15 times rate enhancement.

The amount of iodine produced appeared to be independent of the amount of potassium iodide present, once a minimum level was surpassed. The amount of carbon tetrachloride however had a significant influence. Very low concentrations of carbon tetrachloride resulted in a minimal enhancement of iodine production. On the other hand high concentrations of carbon tetrachloride produced a solvent which was unable to support efficient cavitation due to its high vapour pressure.

Alippi et al[42] investigated the sonolysis of aqueous potassium iodide solutions with carbon tetrachloride, trichloromethane and dichloromethane additions. Ultrasound was shown to enhance the rate of carbon tetrachloride/ water decomposition reactions. Controls indicated no reaction occurred in the absence of sonication. Sonication of potassium iodide solution in the absence of carbon tetrachloride only produced small amounts of iodine due to iodide ion oxidation by hydrogen peroxide formed from the ultrasonic decomposition of water.

Addition of carbon tetrachloride to the reaction mixture increases the amount of iodine produced through the liberation of Cl_2 as follows:-

$$CCl_4 + H_2O \rightarrow CO + Cl_2 + 2HCl$$

The liberated chlorine then acts as an oxidant directly

$$2KI + Cl_2 \rightarrow 2KCl + I_2$$

An alternative route via the formation of hypohalous acid is not thought to be the initial source of iodine because of the low acidity of the original solution.

$$Cl_2 + H_2O \rightarrow HCl + HOCl$$
$$HOCl + HCl + 2KI \rightarrow I_2 + 2KCl + H_2O$$

Carbon dioxide was detected amongst the decomposition products and it was suggested that it could be formed via a phosgene route.

$$CCl_4 + H_2O \rightarrow COCl_2 + 2HCl$$

$$COCl_2 + H_2O \rightarrow CO_2 + 2HCl$$

The amount of iodine formed could not be directly linked to the decomposition of carbon tetrachloride in water simply because of the many other side reactions involved. The sonolysis reactions with trichloromethane and dichloromethane did not produce chlorine (see earlier) and thus iodine formation in these systems was negligible.

Petrier et al[43] compared high frequency 514kHz sonication to the more commonly used lower frequency of 20kHz for the generation of free radicals in the sonolysis of aqueous solutions under argon and oxygen atmospheres. In these studies the formation of triiodide from the sonolysis of potassium iodide was found to be greater under oxygen at higher frequencies. Hydrogen peroxide formation was also monitored and confirmed the result obtained with potassium iodide. In general the higher frequency produced a faster rate of reaction.

The greater efficiency for radical production achieved at high frequency was thought to be due to the collapse time of the cavitation bubbles. This is shorter at the higher frequency. Thus $OH^{\cdot}$ radicals formed in the cavitation bubble are ejected, soon after generation, into the bulk solution thus allowing greater hydrogen peroxide formation and potassium iodide oxidation. At 20kHz radicals have a longer time within the cavitation bubbles thus allowing other reaction pathways e.g. recombination before they enter the bulk solution.

Oxygen is a radical scavenger it will readily react with the H· radicals to form the hydroperoxy radical HOO·. Therefore at lower frequencies, with the longer retention times of radicals within cavitation bubbles, the close contact of the hydroperoxyl radicals with the hydroxyl radicals allows the following reaction to take place:-

$$HO\cdot + \cdot OOH \rightarrow H_2O + O_2$$

At higher frequencies the much reduced retention time of the radicals within the cavitation bubble lowers the probability of scavenging of the OH· radicals by ·OOH radicals. Thus an enhanced rate under oxygen is observed as the H· radicals are removed and the free OH· radicals are sent into the bulk solution.

3.3 THE USE OF FERROUS ION AS A DOSIMETER FOR SONOCHEMISTRY

Oxidation of ferrous ion (Fe^{2+}) to ferric ion (Fe^{3+}) has been used as a dosimeter within radiation chemistry for many years. It was Weiss[44] et al who initially brought to attention the Fricke solution as a dosimeter for use with γ-rays. It was found that the Fricke ferrous sulphate dosimeter is easy to use, reproducible, useful over a wide range of γ-ray intensities and independent of wavelength, temperature and pressure variations. The Fricke solution is $FeSO_4.7H_2O$ or $Fe(NH_4)_2(SO_4)_2.6H_2O$ dissolved in dilute H_2SO_4 with sodium chloride. The chloride ions seem to inhibit oxidation of Fe^{2+} by organic impurities in the system.

It is known that when water is irradiated with X-rays or α-particles H· and OH· radicals[45] are produced. Recombination of the radicals to H_2O will be the major reaction although some hydrogen peroxide may also form. However any hydrogen peroxide formed will then react with either H$\cdot$ or OH$\cdot$ radicals or any oxygen present in solution.

It is thought that a maximum steady state concentration of hydrogen peroxide is reached due to the competitive reaction between hydrogen peroxide formation and its decomposition. H$\cdot$ radicals are very strongly reducing whilst OH$\cdot$ radicals are very strong oxidising agents. We have already seen that addition of I^- will react with OH$\cdot$ to give OH^- and I_2. In the Fricke dosimeter the addition of Fe^{2+} will give the oxidised Fe^{3+} ion via reaction with the OH$\cdot$ radical.

In recent years the Fricke dosimeter has been adapted for use as a monitoring device for sonicated systems.

3.4 EXPERIMENTAL CONDITIONS

3.4.1 POTASSIUM IODIDE DOSIMETER

The standard reaction conditions were employed as quoted in section 2.1.1.

Reaction Vessel Alterations

The standard reaction conditions were employed as quoted in section 2.1.1. However the reaction vessels employed were a Rosett cell and dimple cell with the sonic probe system and a 250cm^3 conical flask, 100cm^3 conical flask and 100cm^3 round bottomed flask with the sonic bath system. A series of glass tubes of varying diameters were used with the pentagonal tube reactor when it was employed as a batch system.

Volume Alterations

The standard reaction conditions were employed as quoted in section 2.1.1. However the volumes employed were altered from 27.5cm^3, 55cm^3 and 110cm^3 with CCl_4 and 25cm^3 without CCl_4. For the stationary tube reactor volumes of potassium iodide solution corresponding to the tube diameter were studied as follows:-

1730.0cm^3 - No Glass Vessel, 70.0mm diameter
742.5cm^3 - 51.5 mm diameter tube
517.0cm^3 - 45.0 mm diameter tube
330.0cm^3 - 35.5 mm diameter tube
187.0cm^3 - 26.5 mm diameter tube
71.5cm^3 - 16.0 mm diameter tube
13.2cm^3 - 7.0 mm diameter tube

Horn Alterations

The standard reaction conditions were employed as quoted in section 2.1.1. However the sonic horns were altered from the 1.2cm diameter cylindrical horn with a tip area of 1.13cm^2, to the 0.6 cm diameter probe tip (area 0.28cm^2) and the 0.3cm diameter probe tip (area 0.071cm^2).

Power alterations

The standard reaction conditions were employed as quoted in section 2.1.1. However the probe settings were altered to 2,4,6 and 8 with their corresponding power outputs of 6%, 10%, 14% and 20%.

TEMPERATURE ALTERATIONS

Sonicated Oxidation

The standard reaction conditions were employed as quoted in section 2.1.1 but the temperature employed was altered as follows:- 25°C, 35°C, 45°C and 55°C.

Thermal Oxidation

The standard thermal reaction was employed, see section 2.1.2, but the temperatures were altered as follows:- 25°C, 35°C, 45°C, 55°C and 65°C.

DISSOLVED GASES

The standard reaction conditions were employed as quoted in section 2.1.1 but the reactions were repeated without bubbling air into the system and with added air and also with added argon.

FLOW SYSTEMS

Tube Reactor

See Section 2.1.3.

Push-Pull Reactor

See Section 2.1.3.

3.4.2 FRICKE DOSIMETER

The standard reaction conditions were employed as quoted in section 2.1.4.

Effect of Aeration

The standard reaction conditions were employed as quoted in section 2.1.4 but the reaction was performed with and without aeration.

Reaction Vessel Alterations

The standard reaction conditions were employed as quoted in section 2.1.4 but the reaction vessels employed were the Rosett cell and a dimple cell with the sonic probe system and a 250cm^3 conical flask, 100cm^3 conical flask and a 100cm^3 round bottomed flask with the sonic bath system.

Volume Alterations

The standard reaction conditions were employed as quoted in section 2.1.4 but the reaction volumes were altered from 25cm^3, 50cm^3 to 100cm^3.

Horn Alterations

The reaction conditions as stated in section 2.1.4 were followed but 3 horns were compared to one another. The 1.2cm diameter horn (area 1.13cm^2) was compared to the 0.6cm diameter probe tip (area 0.28cm^2) and the 0.3cm diameter probe tip (area 0.071cm^2).

Power Alterations

The standard reaction conditions were employed as quoted in section 2.1.4 but the probe settings were altered from 2,4,6 and 8, with their respective power outputs of 6%, 10%, 14% and 20%.

3.4.3 CALORIMETRY

Calorimetry can be used to measure the amount of ultrasonic power entering a reaction system by determining the temperature rise within the system in the first few moments of sonication. Calorimetric measurements were made by following the procedure described in section 2.1.5.

3.5 ANALYSIS CONDITIONS

3.5.1 Formation of the Iodine Beer Lambert Plot

Initially a diluted solution of 30% w/v (100 vol) solution of hydrogen peroxide was standardised by titration. From the original concentrated solution the dilute solution of hydrogen peroxide necessary for the Beer Lambert could be prepared. Titration of the iodine liberated from potassium iodide by hydrogen peroxide against a standard solution of sodium thiosulphate was used to determine the molarity of the peroxide.

Titrations

The titration was performed as follows:

10cm^3 of the 30w/v hydrogen peroxide was taken and diluted to 250cm^3 with distilled water, 10cm^3 of this solution was then taken and diluted further to 100cm^3. This second solution was titrated against 0.1M sodium thiosulphate employing the following method.

25cm^3 of diluted hydrogen peroxide solution was placed into a conical flask. 25cm^3 of 2M sulphuric acid, 10cm^3 of 10% potassium iodide solution and 3 drops of 3% ammonium molybdate (VI) were also added to the flask. This solution was then titrated against a standard solution of 0.1M sodium thiosulphate, prepared from 6.21g sodium thiosulphate in 250cm^3 of distilled water, until a pale straw coloured solution was obtained. A few drops of starch were added at this point and titration was continued until 2 results were obtained within 0.1cm error.

Dilutions

The 1/250 solution of peroxide was 0.0366M in strength

The 1/25 solution of peroxide was 0.366M in strength

The 30 w/v original solution must therefore have been 9.15M.

A hydrogen peroxide solution of 0.012M was required therefore the 0.0366M solution had to be diluted by a factor of 3.11.

Beer Lambert

To five 10cm^3 volumetric flasks 5cm^3 of 4% potassium iodide solution was added. 1,2,3,4 and 5cm^3 of the 0.012M solution of hydrogen peroxide was added to each of these flasks. The solutions were diluted to 10cm^3 with distilled water. 1cm^3 of CCl_4 was added to each flask and the solutions were left to stand for 30 minutes. After this time all the solutions darkened with the formation of free iodine and were diluted by a factor of fifty. UV/ Visible spectra were obtained and a Beer Lambert plot of Absorbance against Iodine concentration was drawn. The iodine concentration was taken to equal the hydrogen peroxide added as 1M of hydrogen peroxide will produce 1M of iodine and in this experiment the free iodine can only come from hydrogen peroxide oxidation and not via any other oxidative route. Air oxidation is sufficiently slow at room temperature to have no significant effect on the amount of free iodine obtained by this experiment.

The Hydrogen peroxide concentration employed 0.012M this was diluted by 10 in the volumetric flask to give 1.2×10^{-3}M solution which after standing was diluted further by a factor of 50 to give a 2.4×10^{-5}M solution.

All solutions were analysed by UV/ Visible spectroscopy and the absorbance of iodine at 356nm was noted.

UV/ Visible spectroscopic results

UV Absorption	Conc I_2mol dm^{-3}
0	0
0.32	2.4×10^{-5}
0.66	4.8×10^{-5}
0.94	7.2×10^{-5}
1.22	9.6×10^{-5}
1.47	12.0×10^{-5}

3.5.2 Formation of the Ferric Ion Beer Lambert Plot

Solutions of 0.01M ferrous (II) ammonium sulphate and 0.01M ferric (III) ammonium sulphate were prepared in 0.4M sulphuric acid. The Beer Lambert plot was determined in the following manner. Ten 10cm^3 volumetric flasks were taken and 1 to 10cm^3 of ferric (III) ammonium sulphate was added to each consecutive flask. The solutions were then all diluted to 10cm^3 by the addition of ferrous (II) ammonium sulphate. The solutions were again diluted by a factor of 10 and UV/ Visible spectra were obtained and the absorption of the ferric ion was determined at 304nm. At these dilutions ferrous ion does not absorb at this wavelength.

The original 0.01M solutions were diluted twice by 10cm^3 to give final solutions of 1×10^{-4}M.

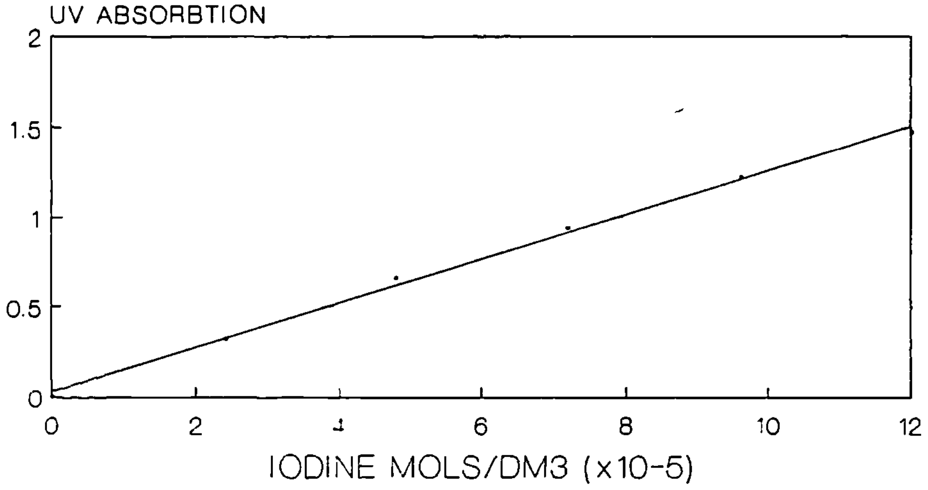
UV/Visible spectometric results

UV Absorption	**Fe^{3+} mol dm^{-3}**
0	0
0.19	$1.0x10^{-4}$
0.39	$2.0x10^{-4}$
0.60	$3.0x10^{-4}$
0.80	$4.0x10^{-4}$
1.04	$5.0x10^{-4}$
1.24	$6.0x10^{-4}$
1.44	$7.0x10^{-4}$
1.67	$8.0x10^{-4}$
1.86	$9.0x10^{-4}$
2.00	$10.0x10^{-4}$

BEER LAMBERT PLOTS

IODINE DOSIMETER

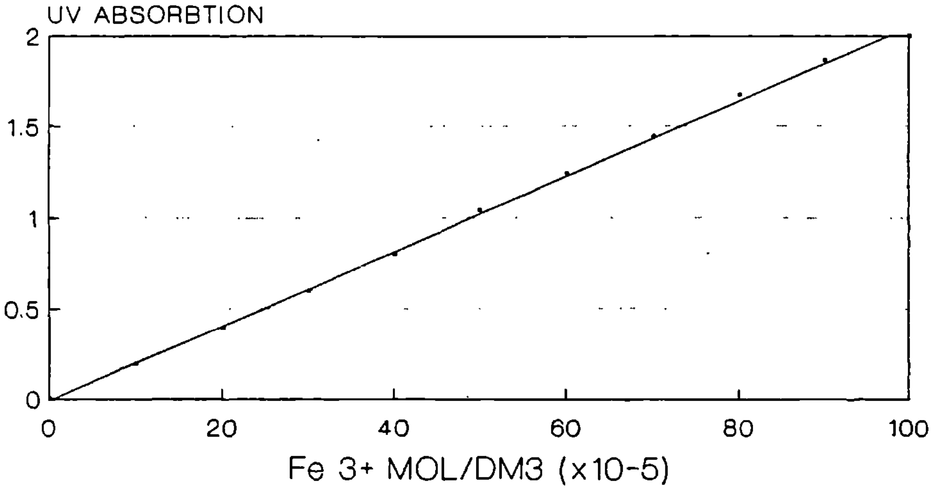
356 NM UV/VISIBLE SPECTROSCOPY



QUARTZ CELLS

FRICKE DOSIMETER

304 NM UV/VISIBLE SPECTROSCOPY



QUARTZ CELLS

3.6 RESULTS/ DISCUSSION

The efficiency of several sonochemical reactors under various reaction conditions have been estimated and compared using 2 chemical dosimeters, the potassium iodide and ferrous ion dosimeters. We have also used the calorimetric method for estimating ultrasonic power input to the various reactors.

3.6.1 POTASSIUM IODIDE DOSIMETER

The oxidation of potassium iodide via the sonolysis of a 4% aqueous solution of potassium iodide is thought to be due to the production of hydrogen peroxide from the homolytic fission of water to hydrogen and hydroxyl radicals and their subsequent reactions.

$$H_2O \rightarrow H^{\cdot} + OH^{\cdot}$$

$$H^{\cdot} + O_2 \rightarrow HO_2^{\cdot} \qquad O^{\cdot} + H_2O \rightarrow 2OH^{\cdot}$$

$$HO_2^{\cdot} + H^{\cdot} \rightarrow H_2O_2 \qquad HO_2^{\cdot} \rightarrow OH^{\cdot} + O^{\cdot}$$

$$2HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \qquad 2OH^{\cdot} \rightarrow H_2O_2$$

The hydrogen peroxide, once formed, oxidises potassium iodide to iodine. This can be observed as a yellow colouration of the clear solution. More accurately this can be monitored by UV/ Visible spectroscopy where iodine absorption may be observed at 356nm.

$$2I^- + H_2O_2 + 2H^+ \rightarrow I_2 + 2H_2O$$

The Iodine dosimeter is simple to prepare, utilise and analyse. It is very sensitive to the amount of hydrogen peroxide present in solution and is consequently a good measure of the efficiency of sonication.

Carbon tetrachloride when added to the reaction increases the rate of iodine liberation by at least 4 times over the corresponding solution without the added CCl_4. The addition does however reduce the reproducibility of the results, although overall trends remain the same. Addition of carbon tetrachloride introduces some side reactions which also lead to the oxidation of potassium iodide to iodine through the production of chlorine radicals on sonolysis.

$$CCl_4 \;\text{->}\; CCl_3\cdot + Cl\cdot$$

$$Cl\cdot + Cl\cdot \;\text{->}\; Cl_2$$

$$2KI + Cl_2 \;\text{->}\; I_2 + 2KCl \quad \text{almost instantaneous}$$

Therefore, in the presence of carbon tetrachloride, the iodine produced is not entirely due to the presence of hydrogen peroxide because of the possible side reactions. Hence results which follow are quoted in terms of iodine yield (mol dm^{-3}) and not hydrogen peroxide generated. A Beer Lambert plot was employed throughout the following experiments for the estimation of concentration and details may be found in the experimental section.

3.6.1.1 EFFECT OF GEOMETRY OF THE REACTION VESSEL

It is always useful to know the performance characteristics of any equipment to be used in order to determine the most efficient way of employing it. It is known that probe systems are able to generate higher intensity ultrasound than sonic baths. However it is not a simple matter to quantify this or to predict how new equipment will compare. We have attempted to use a potassium iodide dosimeter to calibrate sonochemical equipment and thereby give an idea of the relative capabilities of the systems under study.

Ultrasonic Probe

The type of reaction vessel employed with a probe would not be expected to be as important as that used for a sonic bath simply because the probe is placed within the reaction medium itself and there is no barrier between the reaction solution and the sonication device. Rosett cells and dimple cells (see earlier) are often employed because they are designed to produce efficient mixing via acoustic streaming and this permits a more efficient temperature control throughout the reaction mixture.

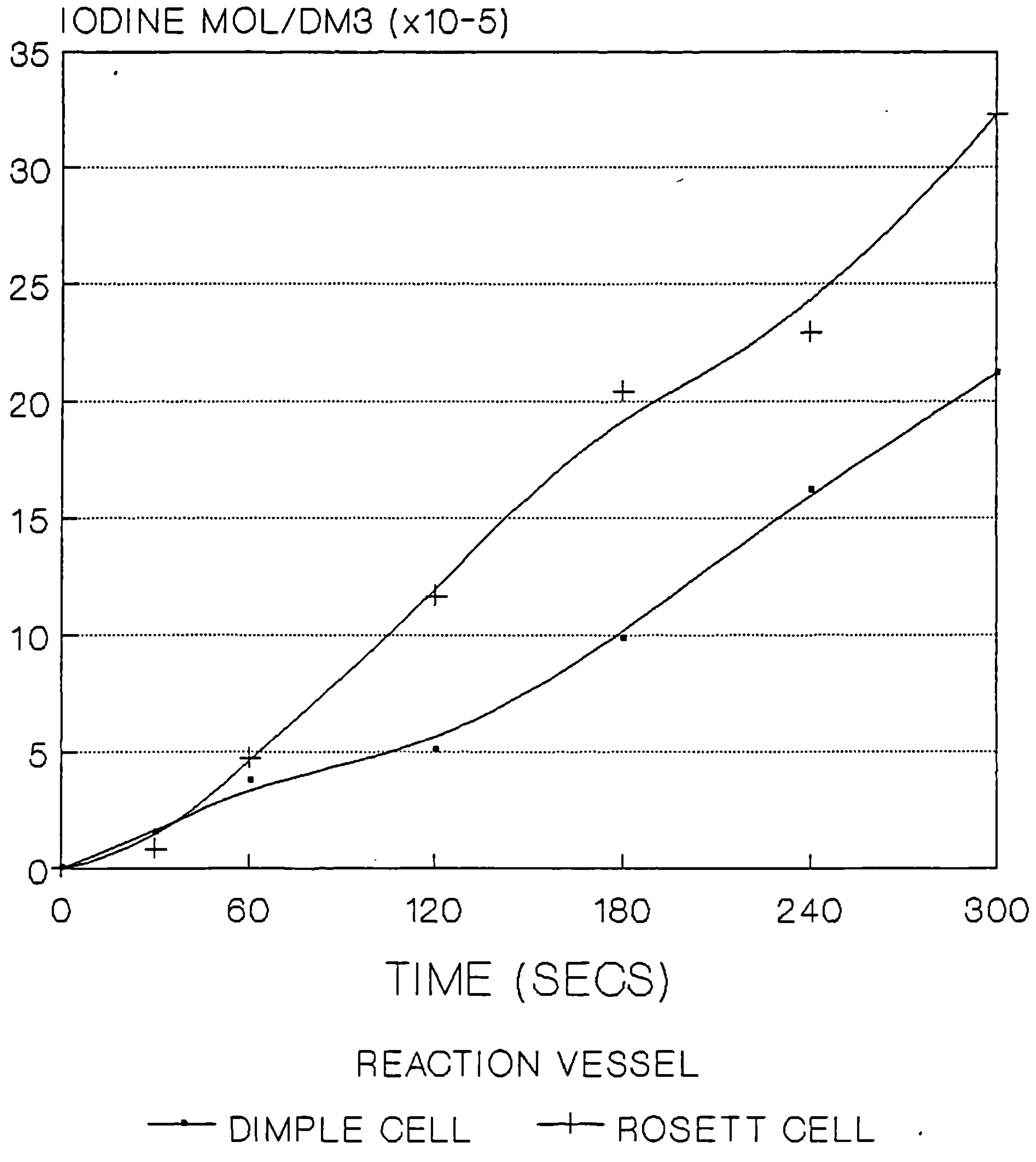
Results obtained (see Table. 3.1 and Fig. 3.1) indicated that the Rosett cell was slightly more efficient than a dimple cell with 32.30×10^{-5}mol dm^{-3} of Iodine formed after 5 minutes sonication compared with 21.19×10^{-5}mol dm^{-3} with the dimple cell.

Table. 3.1 - Effect of reaction vessel changes on I_2mol dm^{-3} on sonication of potassium iodide solution with a sonic probe.

REACTION VESSEL		
Time (secs)	**Dimple Cell**	**Rosett Cell**
30	1.53×10^{-5}	0.82×10^{-5}
60	3.76×10^{-5}	4.70×10^{-5}
120	5.06×10^{-5}	11.64×10^{-5}
180	9.85×10^{-5}	20.44×10^{-5}
240	16.19×10^{-5}	22.90×10^{-5}
300	21.19×10^{-5}	32.30×10^{-5}

Sonicated with a 1.2cm diameter tip probe at setting 4, 10% power output, Sonics and Materials Generator. 110cm^3 reaction volume.

Fig 3.1 - **Effect of reaction vessel changes on Iodine concentration on sonication with a sonic probe**



POTASSIUM IODIDE DOSIMETER

This suggests that for a sonic probe system reaction vessel design does in fact play a part in the sonochemical efficiency of the system.

Ultrasonic Bath

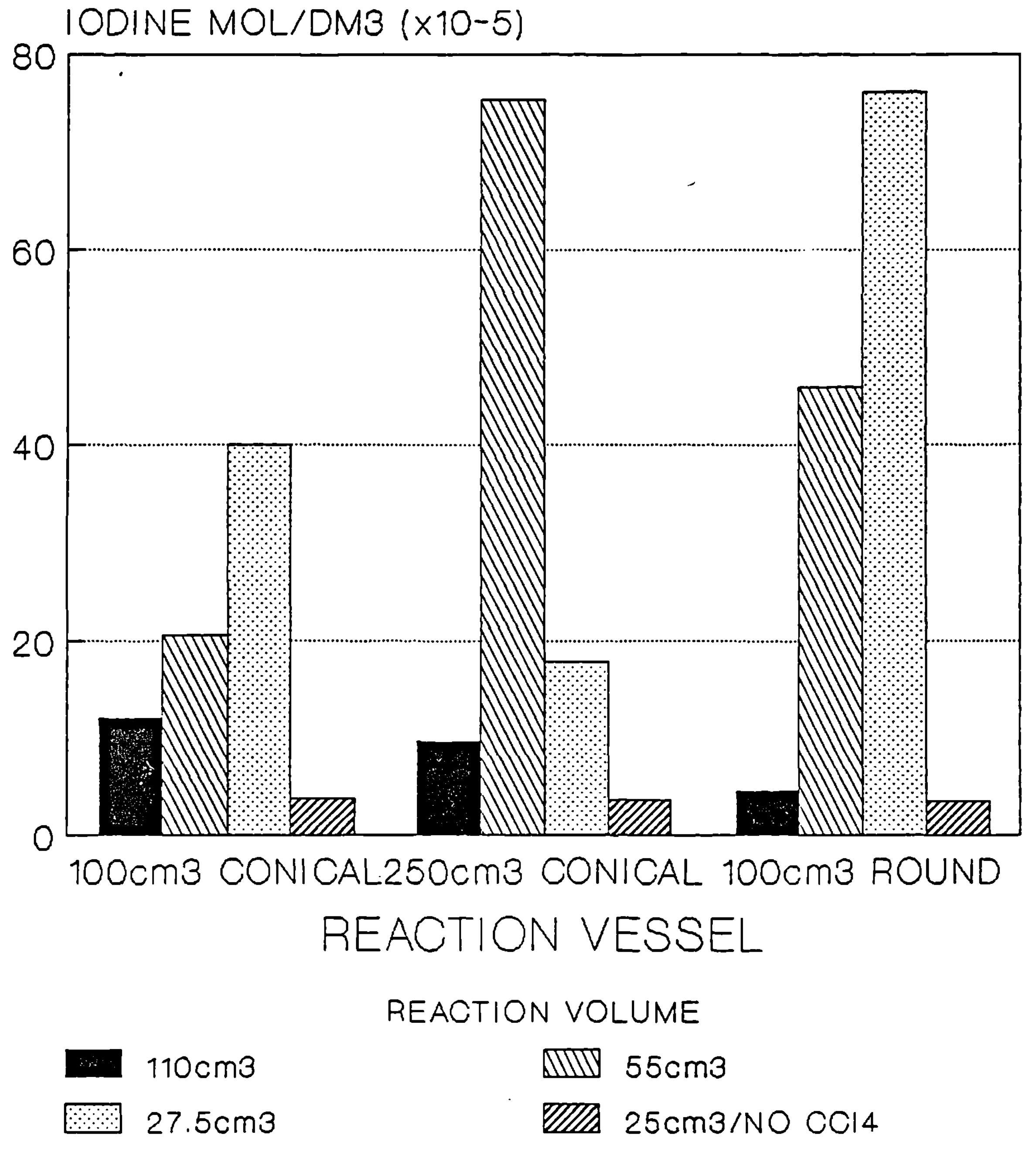
The type of reaction vessel employed and its position are important considerations when using an ultrasonic bath. An ultrasonic cleaning bath normally operates at approximately 38kHz frequency and the power is provided by transducers which are attached to the underside of the base of the bath. The sonic waves travel vertically through the bath medium, are reflected from the surface and set up standing waves. Nodes of high and low intensity are therefore found within the bath as these waves interact to either enhance or cancel each other out, via constructive or destructive interference respectively.

Positioning the base of the reaction vessel within the sonic bath at a point of high ultrasonic intensity is therefore important, as is also the area of exposure of the base of the reaction vessel to the ultrasound. As the ultrasound provided by a sonic bath has to pass through the reaction vessel it is also advisable to employ thin walled vessels to increase the amount of ultrasonic penetration.

From the results obtained in Tables.3.2, 3.3, 3.4 and 3.5, summarised in Fig. 3.2, it can be noted that the type of reaction vessel employed with a sonic bath played a very large part in determining the sonochemical efficiency of the reaction.

For a 110cm^3 reaction volume (Table. 3.2) it can be seen that the most efficient reaction vessel was the 100cm^3 conical flask which produced 12.09x10^{-5}mol dm^{-3} of Iodine in 5 minutes, compared to 9.77x10^{-5} and 4.47x10^{-5}mol dm^{-3} for the 250cm^3 conical flask and the 100cm^3 round bottomed flask respectively. It must be noted that the 100cm^3

Fig 3.2 - Effect of reaction vessel changes on Iodine concentration on sonication with a small sonic bath



POTASSIUM IODIDE DOSIMETER/ 5 MINS

flasks have a capacity large enough to contain 110cm^3 volume of solvent.

Table. 3.2 - Effect of reaction vessel changes on I_2mol dm^{-3} on sonication of potassium iodide solution with a small sonic bath.

	REACTION VESSEL		
Time (secs)	**100cm^3 Conical Flask**	**250cm^3 Conical Flask**	**100cm^3 Round Bottomed Flask**
30	2.00x10^{-5}	1.53x10^{-5}	0.47x10^{-5}
60	2.94x10^{-5}	3.06x10^{-5}	0.83x10^{-5}
120	5.76x10^{-5}	4.33x10^{-5}	1.00x10^{-5}
180	9.40x10^{-5}	4.82x10^{-5}	1.41x10^{-5}
240	10.67x10^{-5}	5.59x10^{-5}	2.47x10^{-5}
300	12.09x10^{-5}	9.77x10^{-5}	4.47x10^{-5}

For 110cm^3 reaction volume, 100cm^3 KI with 10cm^3 CCl_4.

However for 55cm^3 reaction volume (Table. 3.3) it was the 250cm^3 conical flask which provided the most efficient iodine production with 75.35x10^{-5}mol dm^{-3} of iodine produced compared to only 20.59x10^{-5} and 45.88x10^{-5}mol dm^{-3} of iodine in the 100cm^3 conical flask and the 100cm^3 round bottomed flask respectively. This was thought to be due to the depth, 1cm^3, of the potassium iodide solution within the 250cm^3 conical flask closely resembling a quarter wavelength of 38kHz sonic waves in water.

VELOCITY = FREQUENCY x WAVELENGTH

VELOCITY (of sound in water at 25°C) = 1496.7 m/sec

FREQUENCY = 38 000 Hz

Therefore the WAVELENGTH of sound produced in a small sonic bath coupled to water medium is approximately 4cm. Thus a quarter wavelength is approximately 1cm.

Nodes and antinodes are quarter wavelengths apart and antinode to antinode distances are half a wavelength apart. By careful positioning of the conical flask it may be possible to obtain maximum constructive interference within the reaction medium to give the best possible reaction conditions.

Table. 3.3 - Effect of reaction vessel changes on I_2mol dm^{-3} on sonication of potassium iodide solution with a small sonic bath.

	REACTION	VESSEL	
Time (secs)	100cm^3 Conical Flask	250cm^3 Conical Flask	100cm^3 Round Bottomed Flask
30	3.65x10^{-5}	4.59x10^{-5}	2.94x10^{-5}
60	4.94x10^{-5}	13.65x10^{-5}	5.06x10^{-5}
120	13.43x10^{-5}	21.19x10^{-5}	13.28x10^{-5}
180	17.61x10^{-5}	31.18x10^{-5}	23.50x10^{-5}
240	24.10x10^{-5}	55.28x10^{-5}	27.60x10^{-5}
300	20.59x10^{-5}	75.35x10^{-5}	45.88x10^{-5}

For 55cm^3 reaction volume, 50cm^3 KI with 5cm^3 CCl_4.

When the volume of potassium iodide was reduced further to 27.5cm^3 (Table. 3.4) the solution depth in the 250cm^3 conical flask was barely enough to cover the base of the flask. Sonic efficiency was thus reduced with only 17.83x10^{-5}mol dm^{-3} of iodine produced compared to 39.99x10^{-5} for the 100cm^3 conical flask.

The efficiency of the round bottomed flask increased as the reaction volume decreased. This may be due to some sort of 'focusing' effect of the round bottomed flask, which due to the curvature of its walls will generally tend to reflect a proportion of the ultrasonic waves, which may act in a 'positive' manner as the volume decreases. As the reaction volume decreased from 110cm^3, 55cm^3 to 27.5cm^3 the yield of iodine produced during 5 minutes sonication increased from 4.47x10^{-5}, 45.88x10^{-5} to 76.09x10^{-5}mol dm^{-3}.

Table. 3.4 - Effect of reaction vessel changes on I_2mol dm^{-3} on sonication of potassium iodide solution with a small sonic bath.

	REACTION	VESSEL	
Time (secs)	**100cm^3 Conical Flask**	**250cm^3 Conical Flask**	**100cm^3 Round Bottomed Flask**
30	7.53x10^{-5}	2.47x10^{-5}	17.08x10^{-5}
60	14.62x10^{-5}	4.00x10^{-5}	31.18x10^{-5}
120	24.92x10^{-5}	8.80x10^{-5}	36.48x10^{-5}
180	23.95x10^{-5}	8.43x10^{-5}	57.29x10^{-5}
240	47.59x10^{-5}	15.37x10^{-5}	73.48x10^{-5}
300	39.99x10^{-5}	17.83x10^{-5}	76.09x10^{-5}

For 27.5cm^3 reaction volume, 25cm^3 KI with 2.5cm^3 CCl_4.

In the absence of carbon tetrachloride (Table. 3.5) the efficiency of iodine production is reduced considerably by a minimum factor of 5, for all reaction vessel types. Evidence points to the fact that, for this system, height levels of solution within the reaction vessel also play some part in determining sonochemical efficiency.

Table. 3.5 - Effect of reaction vessel changes on I_2mol dm^{-3} on sonication of potassium iodide solution with a small sonic bath.

	REACTION	VESSEL	
Time (secs)	**100cm^3 Conical Flask**	**250cm^3 Conical Flask**	**100cm^3 Round Bottomed Flask**
30	0.29x10^{-5}	-	1.41x10^{-5}
60	0.88x10^{-5}	0.47x10^{-5}	1.41x10^{-5}
120	1.76x10^{-5}	0.94x10^{-5}	1.41x10^{-5}
180	2.23x10^{-5}	1.99x10^{-5}	1.06x10^{-5}
240	3.06x10^{-5}	2.35x10^{-5}	2.35x10^{-5}
300	3.65x10^{-5}	3.51x10^{-5}	3.41x10^{-5}

For 25cm^3 reaction volume, 25cm^3 KI with NO CCl_4.

Tube Reactor

The tube reactor employed in these studies is made of stainless steel with a pentagonal section of 70mm diameter and 32cm in length (see earlier). The transducers are placed along the reactor walls in a series of 3-2-3-2-2 with a total of 12 transducers in all. This arrangement would mean that the highest intensity of ultrasound is found towards the centre of the tube.

As the transducers encircle the tube it is thought that the most appropriate reaction vessel type, when the tube reactor is to be employed as a stationary bath (and not as part of a flow system) would be a glass tubes sealed at one end. Using this system the effect of altering the diameter of the reaction vessel (glass tube) and thereby the volume of potassium iodide solution exposed to irradiation can be quantified.

As a batch reactor, employing glass tubes, this system processes relatively small reaction volumes. The diameter of the glass tubes used as reaction vessels certainly have an influence on sonochemical reaction efficiency (see Table. 3.6 and Fig. 3.3). Reaction efficiencies appeared to alternate from high to low as the diameters of the glass vessels altered. As the diameter altered from 51.5mm, 45mm, 35.5mm, 26.5mm, 16mm to 7mm diameter the amount of iodine produced altered from 3.95×10^{-5}, 16.4×10^{-5}, 8.8×10^{-5}, 20.9×10^{-5}, 3.95×10^{-5} to 10.7×10^{-5}mol dm^{-3} of iodine respectively after 5 minutes sonication.

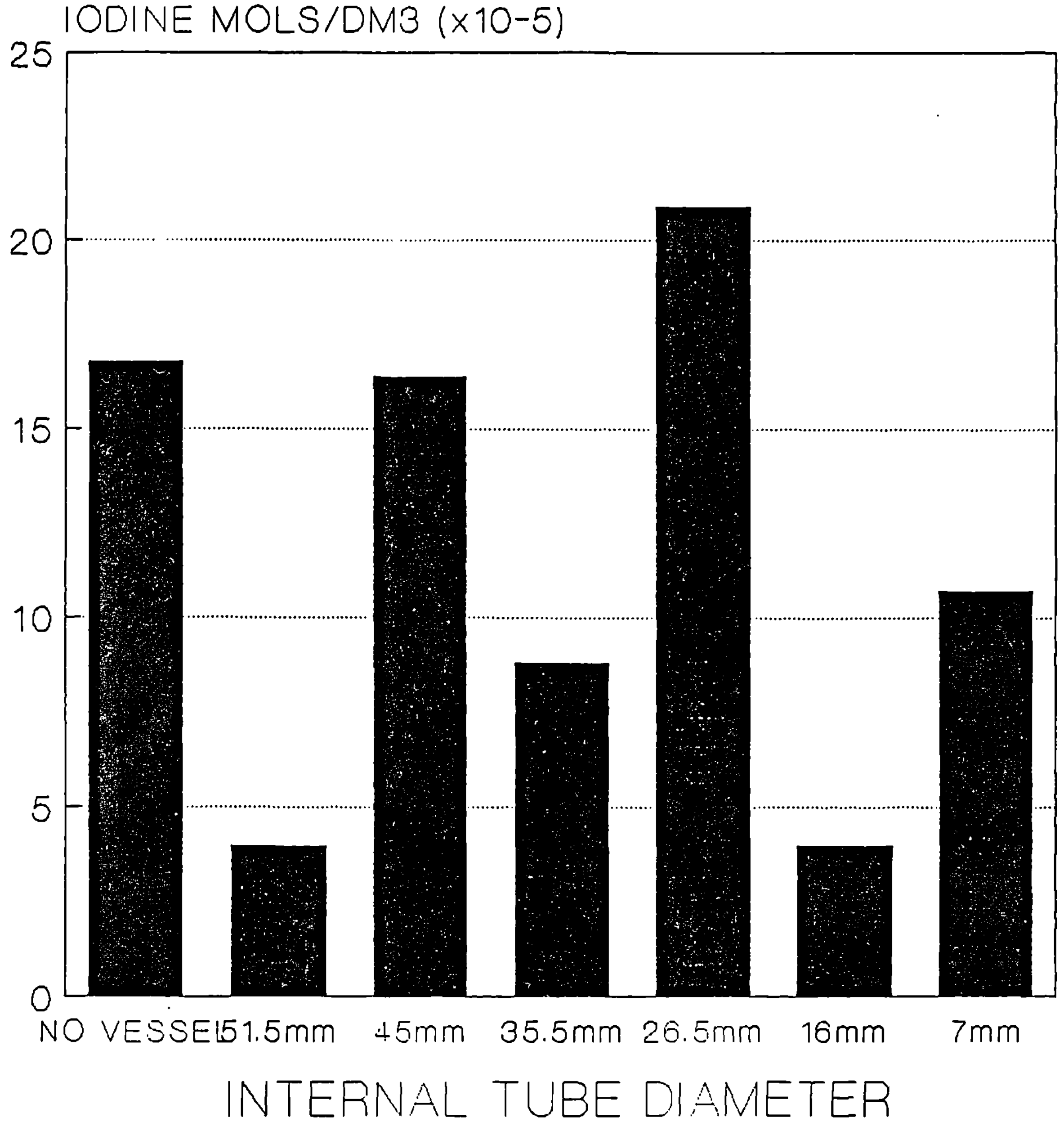
The batch system using the pentagonal tube itself as reactor, *i.e.* with no glass vessel inserted, was very efficient. This arises because the sonic irradiation enters the reaction directly since there are no glass walls for the sonic waves to pass through. In the absence of reaction vessel 16.8×10^{-5}mol dm^{-3} of iodine were produced.

Table. 3.6 - Effect of reaction vessel changes on I_2mol dm^{-3} on sonication of potassium iodide solution with the tube reactor.

INTERNAL TUBE DIAMETER							
Time (secs)	**No Vessel**	**51.5mm**	**45mm**	**35.5mm**	**26.5mm**	**16mm**	**7mm**
30	2.1x10^{-5}	0.8x10^{-5}	0.8x10^{-5}	1.3x10^{-5}	0.5x10^{-5}	0.9x10^{-5}	0.9x10^{-5}
60	3.41 "	1.64 "	3.28 "	2.69 "	4.47 "	1.18 "	1.59"
90	4.94 "	1.94 "	5.37 "	4.92 "	9.03 "	1.76 "	3.17"
120	6.59 "	2.35 "	7.46 "	6.49 "	10.8 "	2.09 "	5.15"
180	10.0 "	3.06 "	10.4 "	8.80 "	14.1 "	2.82 "	6.47"
240	13.4 "	3.51 "	14.9 "	14.2 "	19.4 "	3.06 "	8.43"
300	16.8 "	3.95 "	16.4 "	8.80 "	20.9 "	3.95 "	10.7"

The alternations in reaction efficiency observed may be due to the positioning of the reaction vessel near either alternate high intensity or low intensity nodes of ultrasound as it is irradiated from the walls. It should be noted that the more efficient is the emulsification of carbon tetrachloride within the potassium iodide solution the greater is the iodine production. An example of this was observed with the 7mm diameter tube. Addition of carbon tetrachloride to potassium iodide solution contained within the tube resulted in its settling at the base of the vessel. Application of sonication did not improve its distribution throughout the medium. Addition of a thermocouple wire provided a means for the emulsification of CCl_4 and very high levels of iodine were obtained. The CCl_4 appeared to become attracted to the thermocouple wire and employed it as a method to travel up the tube into the field of sonication thus enhancing emulsification and increasing the amount of iodine generated.

Fig 3.3 - Effect of reaction vessel changes on Iodine concentration on sonication with a tube reactor



POTASSIUM IODIDE DOSIMETER/ 5 MINS

It should also be noted that there will be some variation in glass tube wall thickness which will effect comparisons because it is extremely difficult to produce two tubes with precisely the same uniform thickness of glass.

3.6.1.2 Reaction Volume Alterations

At a constant power input an increase in reaction volume will result in a decrease of ultrasonic intensity per every 1cm^3 volume. This should result in a decrease in iodine yield which should hold true for every type of ultrasonic system employed.

Ultrasonic Probe

Employing a probe with a 1.2cm diameter tip the reaction volumes of 27.5cm^3, 55cm^3 and 110cm^3 were sonicated in a dimple cell. The 27.5cm^3 volume was also sonicated in the absence of carbon tetrachloride. The amounts of iodine detected after 5 minutes sonication were 94.0x10^{-5}, 77.58x10^{-5}, 40.58x10^{-5}mol dm^{-3} respectively and 3.88x10^{-5}mol dm^{-3} in the absence of carbon tetrachloride (see Table. 3.7).

Table. 3.7 - Effect of reaction volume changes on I_2mol dm^{-3} on sonication of potassium iodide solution with a 1.2cm diameter tip sonic probe.

Time (secs)	**27.5cm^3**	**55.0cm^3**	**110cm^3**	**NO CCl_4**
30	17.08x10^{-5}	5.64x10^{-5}	3.70x10^{-5}	0.12x10^{-5}
60	35.06x10^{-5}	11.26x10^{-5}	7.91x10^{-5}	0.47x10^{-5}
120	72.88x10^{-5}	24.99x10^{-5}	14.70x10^{-5}	0.88x10^{-5}
180	91.76x10^{-5}	39.99x10^{-5}	21.78x10^{-5}	1.49x10^{-5}
240	94.00x10^{-5}	56.40x10^{-5}	29.99x10^{-5}	2.59x10^{-5}
300	94.00x10^{-5}	77.58x10^{-5}	40.58x10^{-5}	3.88x10^{-5}

Sonics and Materials Equipment, Setting 5, Power Output 12%.

The highest concentration of iodine was generated in the lowest reaction volume as expected. In the absence of carbon tetrachloride the iodine yield was reduced by at least a factor of 10.

Ultrasonic Bath

Similar results were obtained when sonication was introduced by a small sonic bath. For example the 100cm^3 conical flask (see Table. 3.8 and Fig. 3.2) produced iodine concentrations of 39.99x10^{-5}, 20.59x10^{-5}, 12.09x10^{-5}mol dm^{-3}, for the volumes of 27.5cm^3, 55cm^3 and 110cm^3 respectively, and 3.65x10^{-5}mol dm^{-3} in the absence of carbon tetrachloride (giving an iodine yield enhancement of a minimum factor of 3 when it is included).

Table. 3.8 - Effect of reaction volume changes on I_2mol dm^{-3} on sonication of potassium iodide solution with a small sonic bath.

100cm^3 CONICAL FLASK				
Time (secs)	**27.5cm^3**	**55.0cm^3**	**110cm^3**	**NO CCl_4**
30	7.53x10^{-5}	3.65x10^{-5}	2.00x10^{-5}	0.29x10^{-5}
60	14.62x10^{-5}	4.94x10^{-5}	2.94x10^{-5}	0.88x10^{-5}
120	24.92x10^{-5}	13.43x10^{-5}	5.76x10^{-5}	1.76x10^{-5}
180	23.95x10^{-5}	17.61x10^{-5}	9.40x10^{-5}	2.23x10^{-5}
240	47.59x10^{-5}	24.10x10^{-5}	10.67x10^{-5}	3.06x10^{-5}
300	39.99x10^{-5}	20.59x10^{-5}	12.09x10^{-5}	3.65x10^{-5}

The 250cm^3 conical flask however resulted in a lower iodine yield in the 27.5cm^3 reaction volume than the 55cm^3 reaction volume. This was thought to be due to insufficient depth of solution within the flask resulting in inadequate coupling of the sonic waves (see Table. 3.9).

Table. 3.9 - Effect of reaction volume changes on I_2mol dm^{-3} on sonication of potassium iodide solution with a small sonic bath.

250cm^3 CONICAL FLASK				
Time (secs)	**27.5cm^3**	**55.0cm^3**	**110cm^3**	**NO CCl_4**
30	2.47x10^{-5}	4.59x10^{-5}	1.53x10^{-5}	-
60	3.99x10^{-5}	13.65x10^{-5}	3.06x10^{-5}	0.47x10^{-5}
120	8.80x10^{-5}	21.19x10^{-5}	4.33x10^{-5}	0.94x10^{-5}
180	8.43x10^{-5}	31.18x10^{-5}	4.82x10^{-5}	2.00x10^{-5}
240	15.37x10^{-5}	55.28x10^{-5}	5.59x10^{-5}	2.35x10^{-5}
300	17.83x10^{-5}	75.35x10^{-5}	9.77x10^{-5}	3.51x10^{-5}

The results for the 100cm^3 round bottomed flask followed a similar trend to the 100cm^3 conical flask (see Table. 3.10).

Table. 3.10 - Effect of reaction volume changes on I_2mol dm^{-3} on sonication of potassium iodide solution with a small sonic bath.

100cm^3 ROUND BOTTOMED FLASK				
Time (secs)	**27.5cm^3**	**55.0cm^3**	**110cm^3**	**NO CCl_4**
30	17.08x10^{-5}	2.94x10^{-5}	0.47x10^{-5}	1.41x10^{-5}
60	31.18x10^{-5}	5.06x10^{-5}	0.82x10^{-5}	1.41x10^{-5}
120	36.48x10^{-5}	13.28x10^{-5}	1.00x10^{-5}	1.41x10^{-5}
180	57.29x10^{-5}	23.50x10^{-5}	1.41x10^{-5}	1.06x10^{-5}
240	73.48x10^{-5}	27.60x10^{-5}	2.47x10^{-5}	2.35x10^{-5}
300	76.09x10^{-5}	45.88x10^{-5}	4.47x10^{-5}	3.41x10^{-5}

3.6.1.3 Horn Alterations

The type of horn employed in probe sonication is important when the volume of reaction to be treated is considered.

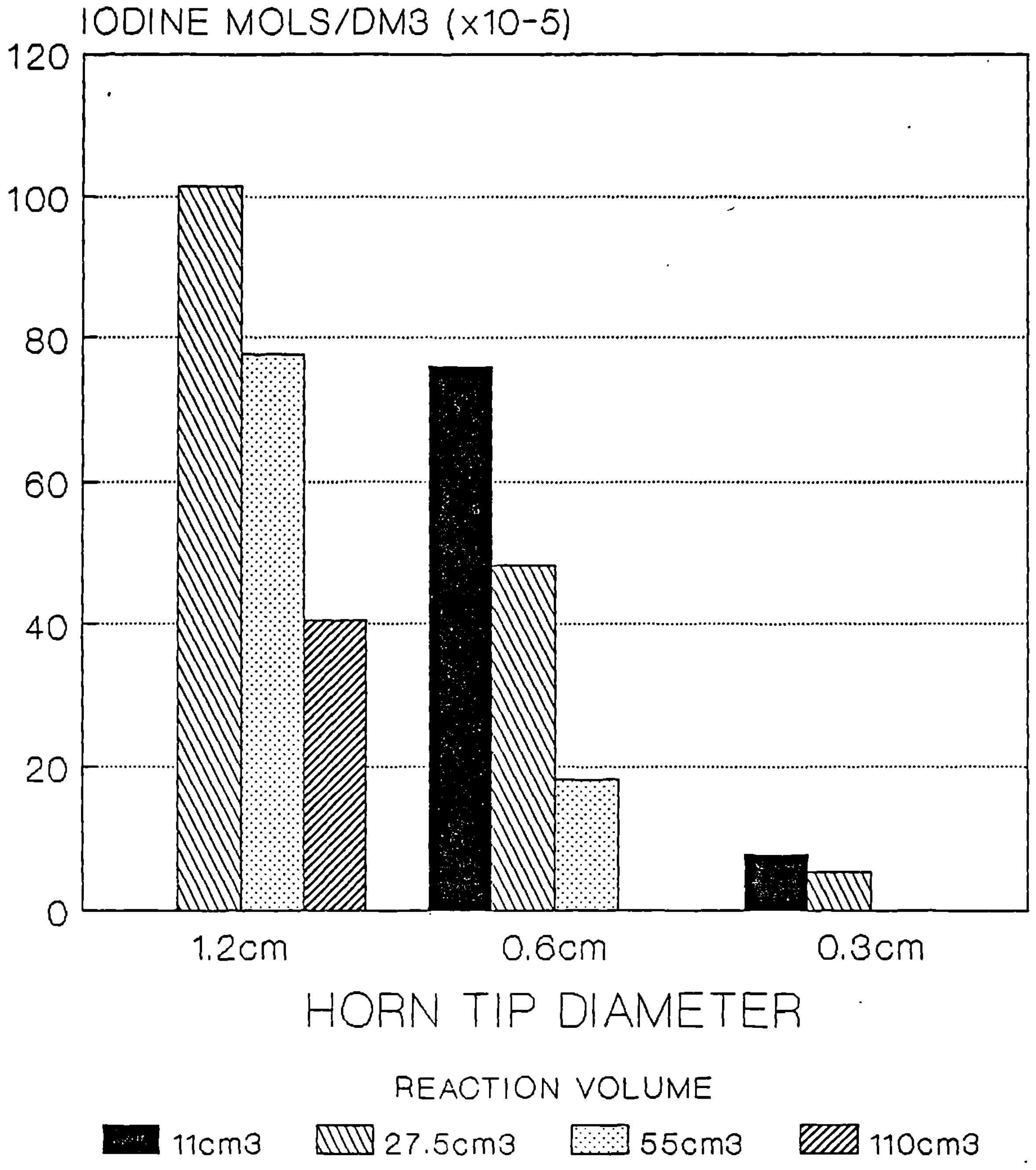
Detachable horns offer amplification of ultrasonic power. Various shapes of horn are available (see earlier Chapter 1) and offer various grades of amplification. The uniform cylindrical horn, end tip diameter 1.2cm, does not magnify the amplitude of ultrasonic vibrations at the end tip. The linear tapered horn will amplify the power output 4-fold (based on the relative areas of its faces) and the exponential taper provides even more amplification.

Although the horns increase the ultrasonic vibrations at the tip thus offering greater power output, the decrease in diameter of the horn end will reduce the volume of the solution affected. The highest intensity of ultrasonic power can be found directly below the horn tip in the 'sonication zone'. Although the greatest amount of cavitation can be found here the resultant micro-streaming and mass transport offers efficient circulation of the solution throughout the ultrasonic field.

For small volumes, for example 10cm^3, a tapered horn of tip diameter 0.3cm with a surface area of 0.071cm^2, would be preferred as this would fit conveniently into the vessel. For larger volumes, *e.g.* 100cm^3, the 1.2cm diameter tip horn with a surface area of 1.13cm^2 would be more reasonable as the increased tip size would also increase the direct sonication area. The 0.6cm diameter horn is of an intermediate size and has a tip surface area of 0.28cm^2 .

The tapered horn with 0.3cm tip produces ultrasound at a higher intensity than horns with larger tips, *i.e.* approximately 130W/cm^2 compared with 30W/cm^2 for the 1.2cm diameter tip. However due to its small size this intensity is not distributed as widely

Fig 3.4 - Effect of horn alterations on Iodine concentration



POTASSIUM IODIDE DOSIMETER/ 5 MINS

within the reaction medium.

A comparison of iodine production after 5 minutes of sonication, with Sonics and Materials equipment setting 4 (10% output), indicated that for the tip areas of 1.13, 0.28 and 0.071cm^2 there was 101.5x10^{-5}, 48.2x10^{-5} and 5.4x10^{-5}mol dm^{-3} of iodine formed (see Table. 3.11 and Fig. 3.4). Reduction in tip area reduces the volume of 'cavitation/ sonic streaming' directly beneath the tip and thereby reduces the volume of reagent directly affected by sonication thus decreasing the efficiency of reaction.

Table. 3.11 - Effect of horn alterations on I_2mol dm^{-3} on potassium iodide sonicated with a sonic probe.

	HORN TIP DIAMETER		
Time (secs)	**1.2 cm**	**0.6 cm**	**0.3 cm**
10	3.05x10^{-5}	0.35x10^{-5}	0.24x10^{-5}
20	8.13x10^{-5}	2.82x10^{-5}	0.47x10^{-5}
30	12.68x10^{-5}	3.53x10^{-5}	0.65x10^{-5}
60	27.60x10^{-5}	6.06x10^{-5}	1.18x10^{-5}
90	44.69x10^{-5}	10.44x10^{-5}	1.59x10^{-5}
120	51.70x10^{-5}	14.92x10^{-5}	2.23x10^{-5}
180	83.55x10^{-5}	26.86x10^{-5}	3.23x10^{-5}
240	97.73x10^{-5}	36.48x10^{-5}	4.00x10^{-5}
300	101.46x10^{-5}	48.19x10^{-5}	5.41x10^{-5}

27.5cm^3 reaction volume, 25cm^3 KI and 2.5cm^3 CCl_4, Power Output 9%/8%/7% depending upon the horn employed. Employing the Sonics and Materials generator.

Tables.3.12 and 3.13 examine the effect of volume changes on a sonicated reaction with 0.6cm and 0.3cm tip sonic horns. As expected an increase in volume resulted in a decrease in iodine yield.

Table. 3.12 - Effect of volume changes on I_2mol dm^{-3} on potassium iodide solution sonicated with a 0.3cm diameter probe.

0.3cm TIP DIAMETER			
Time (secs)	**11cm^3**	**27.5cm^3**	**11cm^3/ NO CCl_4**
10	0.47x10^{-5}	0.24x10^{-5}	0.35x10^{-5}
20	0.94x10^{-5}	0.47x10^{-5}	0.24x10^{-5}
30	1.41x10^{-5}	0.65x10^{-5}	0.24x10^{-5}
60	3.41x10^{-5}	1.18x10^{-5}	0.47x10^{-5}
90	4.70x10^{-5}	1.59x10^{-5}	0.35x10^{-5}
120	6.94x10^{-5}	2.23x10^{-5}	0.47x10^{-5}
180	7.76x10^{-5}	3.23x10^{-5}	0.53x10^{-5}
240	9.85x10^{-5}	4.00x10^{-5}	0.59x10^{-5}
300	7.76x10^{-5}	5.41x10^{-5}	0.71x10^{-5}

Sonics and Materials Generator, Setting 4, Power Output 6%.

Table. 3.13 - Effect of volume changes on I_2mol dm^{-3} on potassium iodide solution sonicated with a 0.6cm diameter probe.

0.6cm TIP DIAMETER			
Time (secs)	**11cm^3**	**27.5cm^3**	**55cm^3**
10	3.17x10^{-5}	0.35x10^{-5}	0.58x10^{-5}
20	6.47x10^{-5}	2.82x10^{-5}	1.11x10^{-5}
30	10.22x10^{-5}	3.53x10^{-5}	1.71x10^{-5}
60	22.31x10^{-5}	6.06x10^{-5}	3.53x10^{-5}
90	31.71x10^{-5}	10.44x10^{-5}	5.70x10^{-5}
120	48.19x10^{-5}	15.29x10^{-5}	7.29x10^{-5}
180	58.78x10^{-5}	27.00x10^{-5}	10.59x10^{-5}
240	58.78x10^{-5}	36.48x10^{-5}	16.34x10^{-5}
300	76.09x10^{-5}	48.19x10^{-5}	18.05x10^{-5}

Sonics and Materials Generator, Setting 4, Power Output 8%.

3.6.1.4 Power Alterations

It would be expected that an increase in power input should increase cavitation and thereby increase the amount of iodine produced. At sufficiently high powers a point will be reached where the amount of cavitation itself acts as a barrier to energy transfer, the system 'decouples' and additional power input may then reduce the yield of iodine.

$110cm^3$ of potassium iodide solution was sonicated in a Rosett cell with a 1.2cm tip at power settings of 2, 4, 6 and 8 (outputs of 6%, 10%, 14% and 20% respectively). For these reactions no decoupling occurred and more iodine was produced at the higher power levels. $13.5x10^{-5}$, $32.3x10^{-5}$, $41.0x10^{-5}$ and $51.0x10^{-5}mol\ dm^{-3}$ respectively (see Table. 3.15). Similar results were obtained with a dimple cell (see Table. 3.14 and Fig. 3.5).

Table. 3.14 - Effect of applied power on $I_2mol\ dm^{-3}$ on the sonicated oxidation of potassium iodide.

DIMPLE CELL				
Time (secs)	**Setting 2**	**Setting 4**	**Setting 6**	**Setting 8**
30	$1.18x10^{-5}$	$1.49x10^{-5}$	$2.35x10^{-5}$	$1.18x10^{-5}$
60	$2.53x10^{-5}$	$3.76x10^{-5}$	$4.70x10^{-5}$	$7.06x10^{-5}$
120	$5.66x10^{-5}$	$5.06x10^{-5}$	$11.79x10^{-5}$	$16.41x10^{-5}$
180	$10.00x10^{-5}$	$9.85x10^{-5}$	$18.20x10^{-5}$	$24.62x10^{-5}$
240	$12.01x10^{-5}$	$16.19x10^{-5}$	$28.80x10^{-5}$	$38.20x10^{-5}$
300	$14.32x10^{-5}$	$21.19x10^{-5}$	$37.00x10^{-5}$	$49.39x10^{-5}$

For $110cm^3$ reaction volume, $100cm^3$ KI and $10cm^3$ CCl_4. Sonicated with a 1.2cm diameter tip probe.

Table. 3.15 - Effect of applied power on I_2mol dm^{-3} on the sonicated oxidation of potassium iodide.

ROSETT CELL				
Time (secs)	Setting 2	Setting 4	Setting 6	Setting 8
30	1.41x10^{-5}	0.82x10^{-5}	7.29x10^{-5}	2.35x10^{-5}
60	2.91x10^{-5}	4.70x10^{-5}	11.04x10^{-5}	7.06x10^{-5}
120	5.76x10^{-5}	11.64x10^{-5}	11.79x10^{-5}	13.43x10^{-5}
180	8.56x10^{-5}	20.44x10^{-5}	22.90x10^{-5}	23.50x10^{-5}
240	11.49x10^{-5}	22.90x10^{-5}	31.71x10^{-5}	35.21x10^{-5}
300	13.50x10^{-5}	32.30x10^{-5}	41.03x10^{-5}	51.47x10^{-5}

For 110cm^3 reaction volume, 100cm^3 KI and 10cm^3 CCl_4. Sonicated with a 1.2cm diameter tip probe.

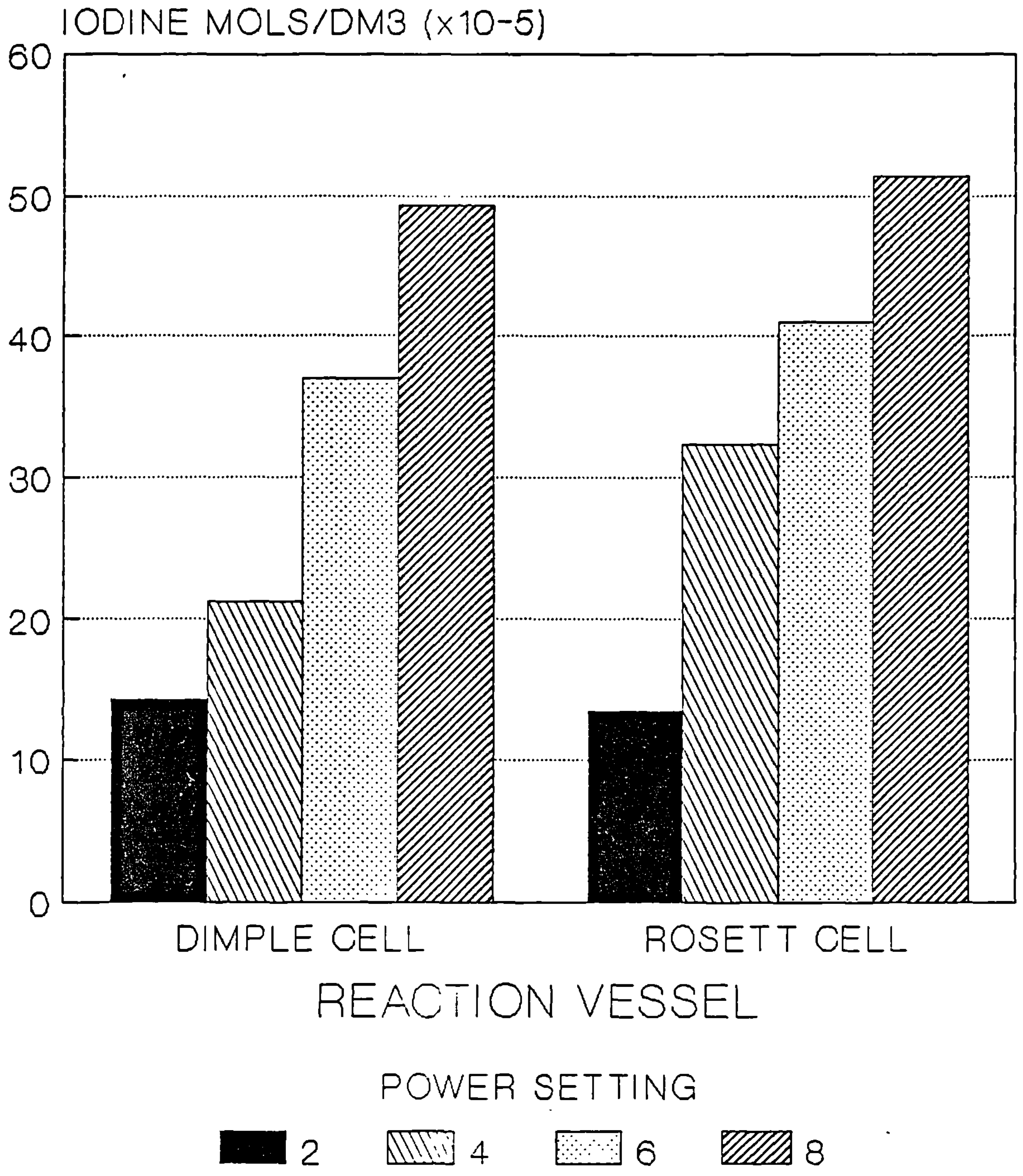
3.6.1.5 Temperature Alterations

Sonicated Oxidation

Unlike conventional thermal reactions, where an increase in temperature results in an increase in reaction rate, ultrasonic reactions are generally favoured by a temperature decrease. As the temperature is increased reagent vapour pressure also increases and any cavitation bubbles formed become quickly filled with vapour and the energy of cavitational collapse is decreased.

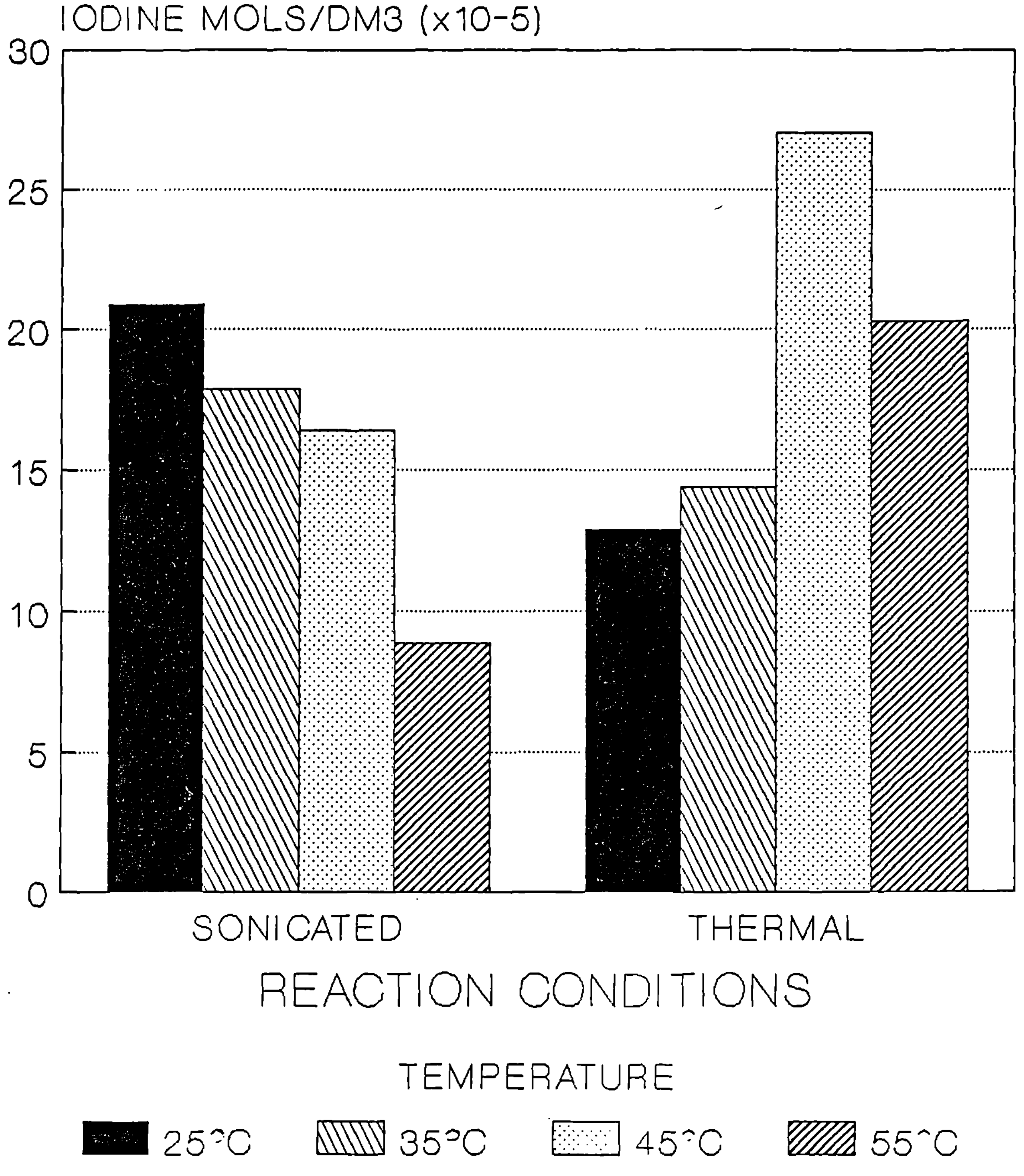
Table. 3.16 and Fig. 3.6 demonstrate that as the solutions were sonicated at setting 4 (10% output) and the reaction temperature was increased from 25°C to 55°C the level of iodine formed decreased as follows 20.89x10^{-5}, 17.9x10^{-5}, 16.4x10^{-5} and 8.88x10^{-5}mol dm^{-3} for temperatures of 25°C, 35°C, 45°C and 55°C respectively, in accord with the trend expected for cavitationally activated reactions.

Fig 3.5 - Effect of applied power on Iodine concentration



POTASSIUM IODIDE DOSIMETER/ 5 MINS

Fig 3.6 - Effect of changes in reaction temperature on Iodine concentration



POTASSIUM IODIDE DOSIMETER/ 5 MINS

Table. 3.16 - Effect of changes in reaction temperatures on I_2mol dm^{-3} on the sonicated oxidation of potassium iodide.

	TEMPERATURE			
Time (secs)	**25°C**	**35°C**	**45°C**	**55°C**
30	4.12×10^{-5}	2.82×10^{-5}	2.23×10^{-5}	2.09×10^{-5}
60	5.76×10^{-5}	5.53×10^{-5}	4.23×10^{-5}	3.41×10^{-5}
90	8.80×10^{-5}	7.39×10^{-5}	5.64×10^{-5}	4.23×10^{-5}
120	10.59×10^{-5}	8.95×10^{-5}	8.21×10^{-5}	7.41×10^{-5}
180	12.61×10^{-5}	12.31×10^{-5}	15.74×10^{-5}	5.52×10^{-5}
240	16.79×10^{-5}	16.41×10^{-5}	11.79×10^{-5}	6.35×10^{-5}
300	20.89×10^{-5}	17.90×10^{-5}	16.41×10^{-5}	8.88×10^{-5}

For 110cm^3 reaction volume, 100cm^3 KI and 10cm^3 CCl_4. Sonicated with a 1.2cm diameter tip probe.

Thermal Oxidation

The oxidation of acidified potassium iodide was examined at a range of temperatures between 25°C and 55°C (see Table. 3.17 and Fig. 3.6). After stirring the solution for 60 minutes at the different temperatures employed the quantities of iodine liberated were 12.91×10^{-5}, 14.40×10^{-5}, 27.00×10^{-5} and 20.29×10^{-5}mols dm^{-3} at 25°C, 35°C, 45°C and 55°C respectively. This shows that the oxidation of potassium iodide undergoes normal thermal effects.

It must be also noted that sonication whilst achieving higher iodine concentrations at lower temperatures also reduced the time required to obtain a given level of iodine. At the same temperature yields obtained after only 5 minutes of sonication required some 60 minutes under thermal conditions alone. These results demonstrate the difference between thermal and sonochemical activation.

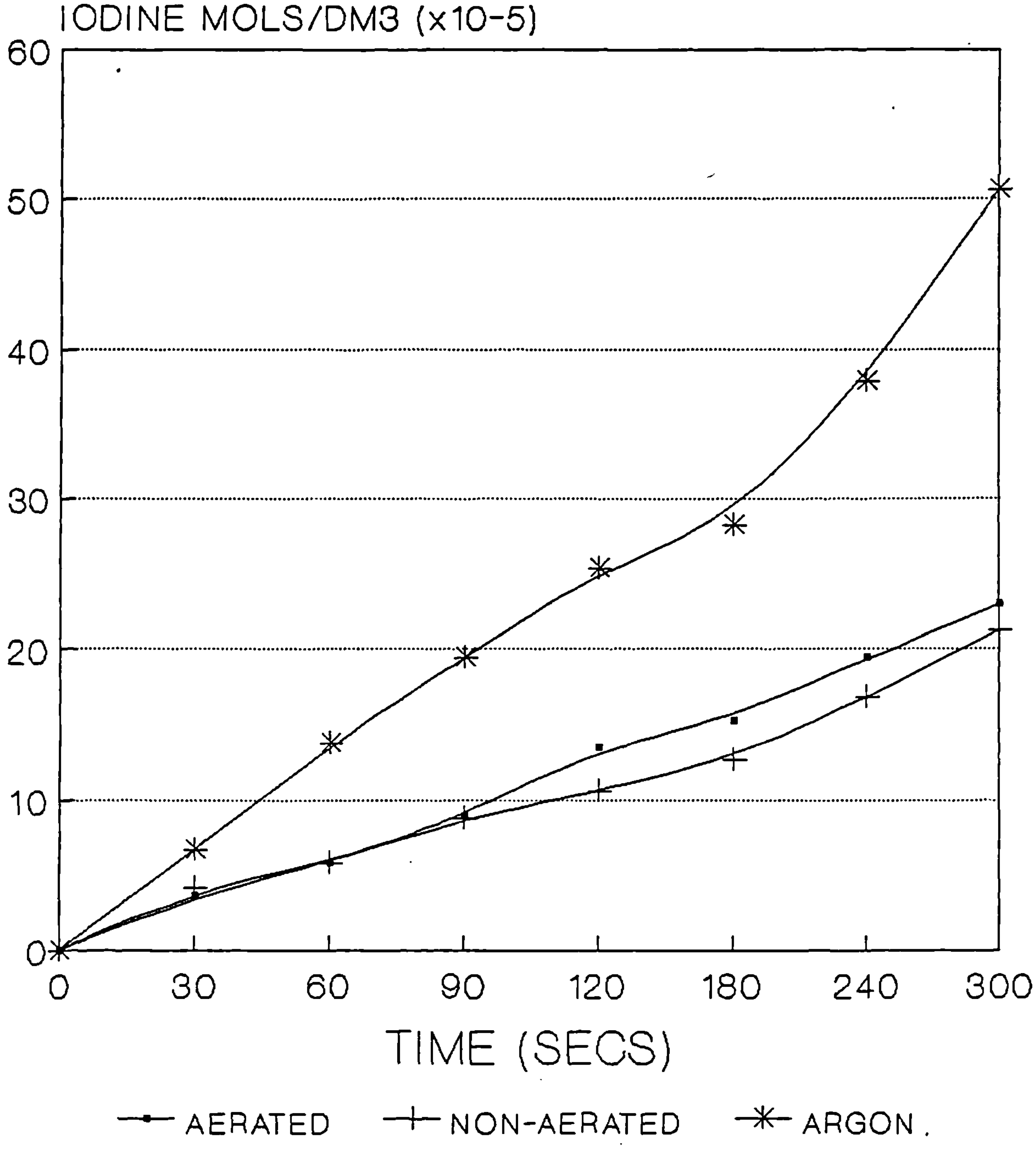
Table. 3.17 - Effect of changes in reaction temperatures on I_2mol dm^{-3} on the thermal oxidation of potassium iodide.

TEMPERATURE				
Time (mins)	**25°C**	**35°C**	**45°C**	**55°C**
5	0.13×10^{-5}	-	0.58×10^{-5}	0.29×10^{-5}
10	0.20×10^{-5}	0.58×10^{-5}	2.06×10^{-5}	1.18×10^{-5}
15	0.29×10^{-5}	1.76×10^{-5}	3.53×10^{-5}	1.47×10^{-5}
30	6.53×10^{-5}	6.17×10^{-5}	10.00×10^{-5}	4.99×10^{-5}
45	9.62×10^{-5}	9.40×10^{-5}	19.99×10^{-5}	12.01×10^{-5}
60	12.91×10^{-5}	14.40×10^{-5}	27.00×10^{-5}	20.29×10^{-5}

3.6.1.6 The Effect of Dissolved Gases

The effect of dissolved gases on sonochemical reactions have been studied for many years. Elpiner[12] suggested that argon catalysed the splitting of water molecules to their hydrogen and hydroxyl radicals. Suslick[6] proposed that the ability of a gas to conduct heat determines whether the rate will be increased or decreased. A gas such as xenon or argon is a poor conductor of heat and so much of the heat generated during cavitation will be retained in the bubble and the rate will be increased. A gas which conducts heat well, such as helium, will dissipate the heat in the bubble and reduce the rate of reaction. We have examined the effect of introducing argon on the sonochemical oxidation of potassium iodide, (see Table. 3.18 and Fig. 3.7).

Fig 3.7 - Effect of changes in the dissolved gas on Iodine concentration



POTASSIUM IODIDE DOSIMETER/ 5 MINS

Table. 3.18 - Effect of changes in the dissolved gas on I_2mol dm^{-3} on the sonicated oxidation of potassium iodide.

DISSOLVED GASES			
Time (secs)	**Aerated**	**Non-Aerated**	**Argon**
30	3.65×10^{-5}	4.12×10^{-5}	6.70×10^{-5}
60	5.76×10^{-5}	5.76×10^{-5}	13.73×10^{-5}
90	8.95×10^{-5}	8.80×10^{-5}	19.40×10^{-5}
120	13.50×10^{-5}	10.59×10^{-5}	25.29×10^{-5}
180	15.29×10^{-5}	12.61×10^{-5}	28.20×10^{-5}
240	19.40×10^{-5}	16.79×10^{-5}	37.90×10^{-5}
300	22.90×10^{-5}	21.19×10^{-5}	50.58×10^{-5}

110cm^3 reaction volume, 100cm^3 KI and 10cm^3 CCl_4. Dimple cell at 25°C with setting 4, power output 10%.

The aerated reaction produced a similar result to the non-aerated reaction. This can be explained by the fact that the non-aerated reaction was not a totally 'closed' system and there must be enough air present to produce an oxidation rate similar to that of a system where air is forcibly bubbled into the medium to replace any lost during the 'degassing' effect of sonication.

Introducing argon into the reaction system does two things. Firstly it removes any air/O_2 present in the solution. This is useful because oxygen is a radical scavenger and can combine with hydrogen radicals to produce peroxy radicals which then go on to scavenge hydroxyl radicals. Secondly argon has poor heat conduction (see above). Both factors should lead to an enhancement of iodine production on the addition of argon. This was confirmed by the production of 22.0×10^{-5}mols dm^{-3} of iodine in 5 minutes under thermal conditions compared to the 50.6×10^{-5}mol dm^{-3} of iodine obtained in the presence of argon, approximately double the amount (see Table. 3.18).

3.6.1.7 Flow Systems

Tube Reactor

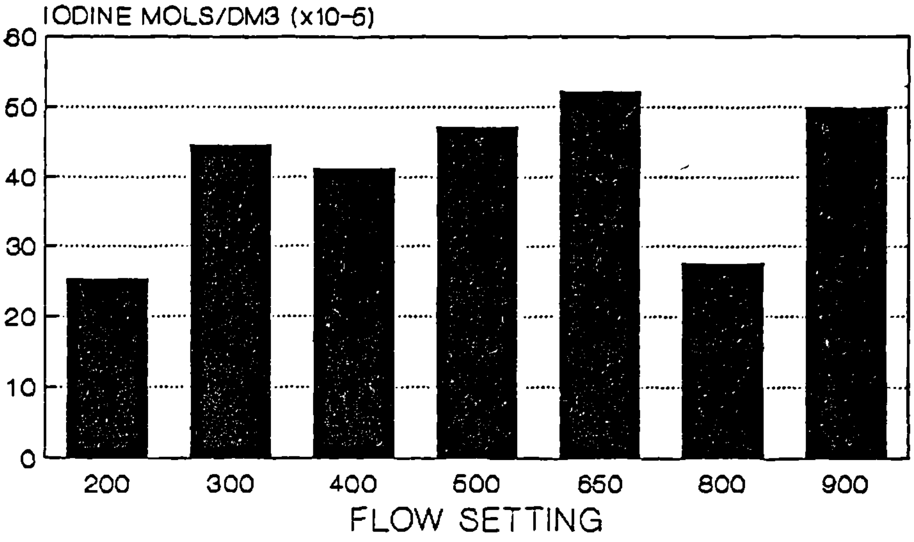
The 'static' volume of the tube reactor is 1730cm^3. When used as a flow system the overall volume processed was 4000cm^3. It can also be noted that problems occur concerning the circulation of a mixture of carbon tetrachloride and aqueous potassium iodide. Carbon tetrachloride being of higher density than the aqueous solution tends to sink to the lowest point of the flow system, this happens to be below the area of sonication. Therefore on slower flow rates there is still a problem of efficiently distributing the carbon tetrachloride which possibly contributes to the lower concentrations of iodine obtained (see Table. 3.19 and Fig. 3.8).

The flow of reactants through the tube reactor and reservoir was controlled by a peristaltic pump employing silicone rubber tubing of 9mm internal diameter. Flow rates varied from a minimum of 1 litre per 8 minutes 30 seconds at setting 200 (residence time 14 minutes 45 seconds) to 1 litre per 1 minute 10 seconds at setting 999 (residence time 2 minutes). Similar levels of iodine were obtained for solutions which were sonicated for a similar length of time, no matter over how many cycles (see Table. 3.19).

The peristaltic pump was set at various rates of flow and the time taken for 1 litre of fluid to be eluted was determined. This then allowed the determination of the flow times/ circuits or cycles around the tube reactor system for a 4 litre solution of potassium iodide. Each flow setting had its own individual cycle time (see p132) however each final reading was taken after 34 minutes for comparison. Thus each sample had the same overall length of time in the sonication area but over a different number of cycles.

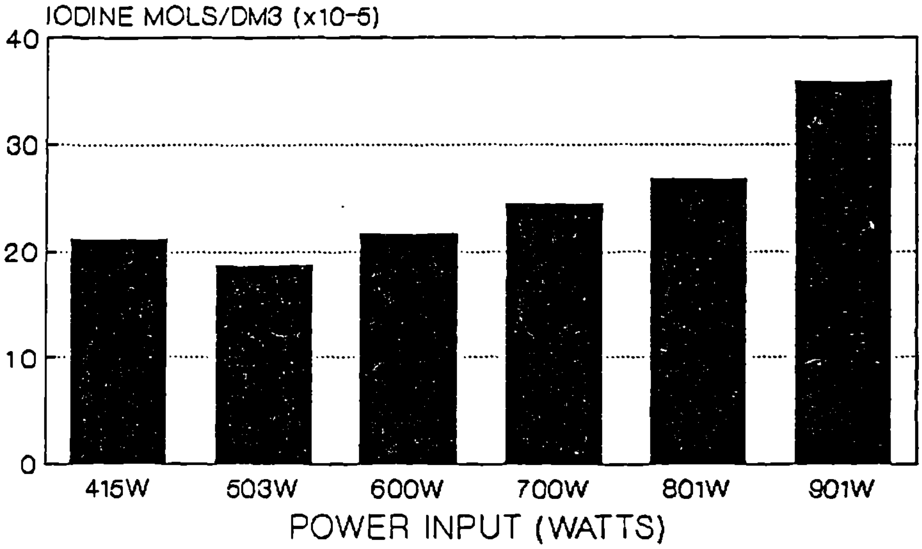
Effect on Iodine concentration due to the presence of a flow system

Fig 3.8 - **Iodine concentration changes due to sonication with the tube reactor flow system**



34 MINS REACTION TIME

Fig 3.9 - **Iodine concentration changes due to sonication with the Push - Pull flow system**



10 MINS REACTION TIME

Table. 3.19 - I_2 mol dm^{-3} changes due to sonication with the Tube Reactor Flow System. Variable Flow Constant Power.

	FLOW SETTING						
CYCLE	**200**	**300**	**400**	**500**	**650**	**800**	**900**
1	25.29*	17.08	1.88	8.80	7.61	2.91	9.40
2		44.69*	41.18	25.29	23.80	8.80	10.59
3			-	41.70	35.21	13.50	17.61
4				47.15*	44.01	18.80	26.48
5					52.22*	22.31	33.50
6						27.60*	39.99
7							49.91*

* - $I_2 x10^{-5}$ Final reading taken after 34 minutes to allow comparison.

Push-Pull Reactor

The Push-Pull equipment employed consisted of a cylinder of titanium metal with a 20kHz transducer fixed to each end (see earlier). The piezoelectric transducers vibrate at ultrasonic frequencies in an 'in and out', 'push-pull' manner. This causes the titanium cylinder to respond by producing radial vibrations at half wavelength distances along its length. We used the reactor mounted vertically although it is possible to use it at any angle.

The Push-Pull machine is of variable power from 415 Watts to 1036 Watts and can be used either with its own reaction vessel or can be placed alone in an existing bath or vat. We operated this system in batch mode. At the maximum power studied of 901Watts, $17.10x10^{-5}$mols iodine per 1 dm^3 were formed after 5 minutes sonication and $35.89x10^{-5}$mol dm^{-3} iodine after 10 minutes (see Table. 3.20 and Fig. 3.9). It must be remembered that in the case of this flow system the reaction volume was 6600cm^3. Also note that an increase in applied power resulted in an increase in iodine formation.

Table. 3.20 - I_2mol dm^{-3} changes due to sonication with the Push-Pull Reactor Flow System. Constant Flow Variable Power.

	POWER INPUT (Watts)					
Time (mins)	415W	503W	600W	700W	801W	901W
1.40	1.06*	1.18*	1.76*	1.18*	-	3.53*
3.20	3.17 "	2.35 "	4.70 "	4.70	5.30*	9.70"
5.00	7.06 "	6.47 "	10.00 "	10.59 "	10.59 "	17.08"
6.40	12.09 "	10.59 "	14.10 "	15.89 "	15.89 "	24.70"
8.20	12.09 "	14.70 "	18.80 "	19.99 "	21.78 "	29.99"
10.00	21.19 "	18.80 "	21.78 "	24.62 "	26.86 "	35.88"

* = x10^{-5}
Fixed rate of flow of 100cm^3 per 10 secs.

3.6.2 FRICKE DOSIMETER

Oxidation of ferrous ion (Fe^{2+}) to ferric ion (Fe^{3+}) has been employed within radiation chemistry for many years. It is both reproducible and quantifiable. The method has been adapted for use as a sonochemical dosimeter in order to compare it with results obtained using the potassium iodide dosimeter.

The ferrous solution employed for this system of calibration was 0.01M ferrous ammonium sulphate in 0.4M sulphuric acid[75]. A Beer Lambert plot was determined from varying solutions containing different concentrations of ferrous (II) ammonium sulphate and ferric (III) ammonium sulphate dodecahydrate. The ferric ion can be identified and quantified from its absorption peak at the UV/ Visible wavelength of 304nm making this method of analysis relatively straight forward.

3.6.2.1 Effect of Aeration

Aeration of the reaction system should produce an increase in ferric ion production as the reaction runs better in the presence of air. There are experimental problems however in the aeration of sonicated reaction volumes of approximately 10cm^3 due to the limited space available for a thermocouple, probe and aeration pipette. For this reason the minimum volume of reaction used was 25cm^3.

On sonication of non-aerated acidic solutions of ferrous ammonium sulphate 6.72×10^{-5} and 8.22×10^{-5}mol dm^{-3} of ferric ammonium sulphate were detected after 2 hours sonication at probe settings of 4 and 6 respectively. Aeration increased the production of ferric ion to 6.47×10^{-5} and 10.93×10^{-5}mol dm^{-3} after only 1 hour at the same power settings (see Table. 3.21).

Table. 3.21 - Fe^{3+}mol dm^{-3} in the presence and absence of aeration.

	NON-AERATED		AERATED	
Time (mins)	**Setting 4**	**Setting 6**	**Setting 4**	**Setting 6**
5	-	-	3.24×10^{-5}	1.62×10^{-5}
10	-	-	3.24×10^{-5}	2.84×10^{-5}
15	2.60×10^{-5}	2.60×10^{-5}	3.65×10^{-5}	3.24×10^{-5}
30	2.99×10^{-5}	2.99×10^{-5}	4.85×10^{-5}	9.32×10^{-5}
45	-	-	6.47×10^{-5}	10.52×10^{-5}
60	5.60×10^{-5}	6.72×10^{-5}	6.47×10^{-5}	10.93×10^{-5}
90	8.09×10^{-5}	8.22×10^{-5}	-	-
120	6.72×10^{-5}	8.22×10^{-5}	-	-

3.6.2.2 The Effect Of Reaction Vessel Geometry

As stated earlier reaction vessels have a significant effect on the efficiency of a sonicated reaction although this has less importance for probe systems than for sonic bath systems.

Ultrasonic Probe

For a probe system it appeared that for the Fricke dosimeter a Rosett cell was slightly more efficient than a dimple cell although the amounts of ferric ions detected were of similar magnitudes 12.10×10^{-5} and 10.93×10^{-5}mol dm^{-3} respectively (see Table. 3.22 and Fig. 3.10). This parallels the results obtained with the potassium iodide dosimeter.

Table. 3.22 -Effect of reaction vessel changes on Fe^{3+}mol dm^{-3} on sonication with a sonic probe.

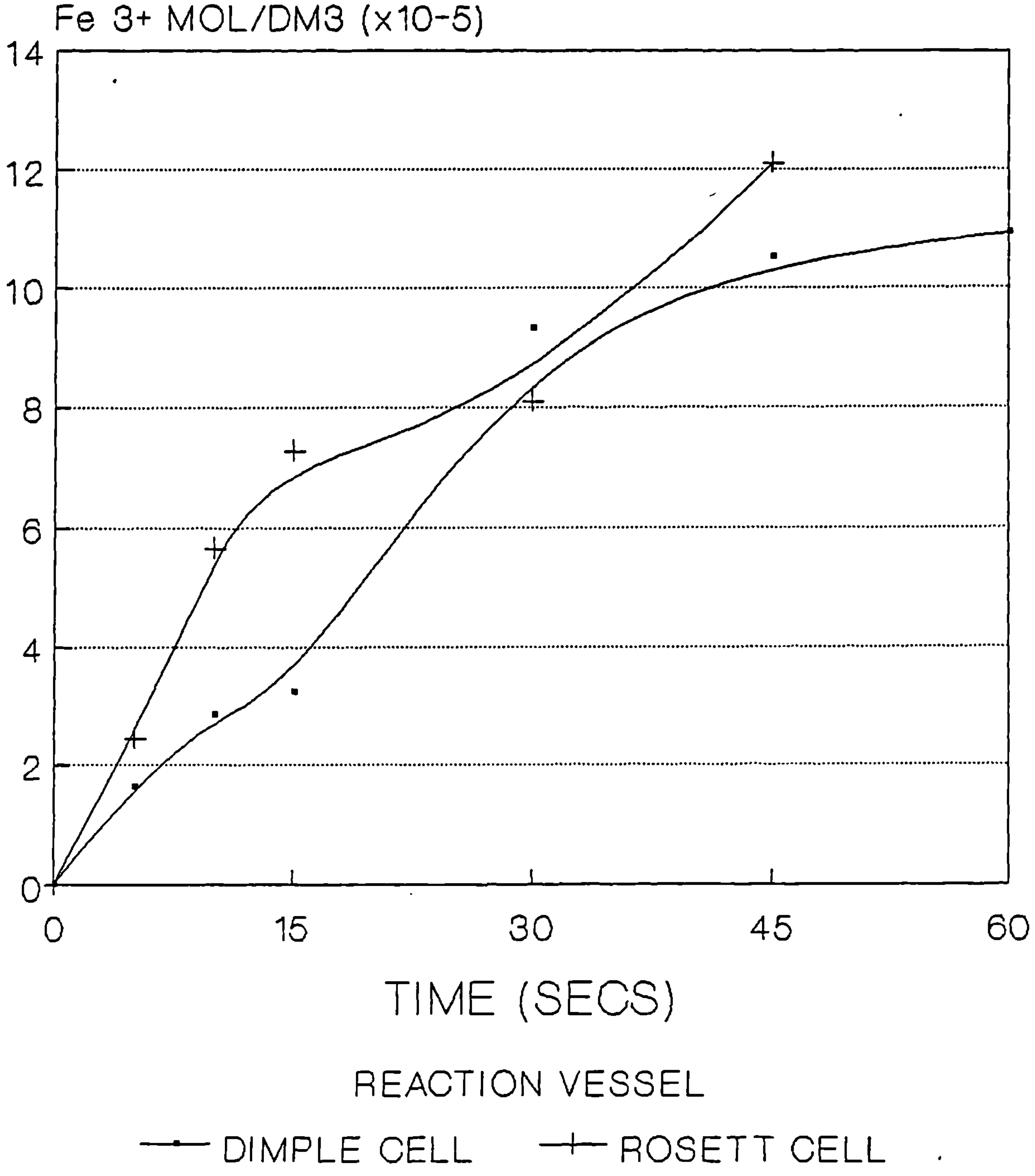
	REACTION VESSEL	
Time (mins)	**Dimple Cell**	**Rosett Cell**
5	1.62×10^{-5}	2.43×10^{-5}
10	2.84×10^{-5}	5.66×10^{-5}
15	3.24×10^{-5}	7.28×10^{-5}
30	9.32×10^{-5}	8.09×10^{-5}
45	10.52×10^{-5}	12.10×10^{-5}
60	10.93×10^{-5}	-

Sonicated with a 1.2cm diameter probe tip at setting 6, 12% power output, Sonics and Materials Generator. 100cm^3 Fe^{2+}/ acid/ air.

Ultrasonic Bath

Sonication of a 100cm^3 reaction volume produced 25.10×10^{-5}mol dm^{-3} of ferric ions in the 250cm^3 conical flask. The 100cm^3 conical flask produced 23.90×10^{-5}mol dm^{-3} of ferric

Fig 3.10 - Effect of reaction vessel changes on Ferric ion concentration on sonication with a sonic probe



FRICKE REACTION

ions and the 100cm^3 round bottomed flask 17.40x10^{-5}mol dm^{-3} of ferric ammonium sulphate (see Table. 3.23 and Fig. 3.11). This follows a similar trend to that observed in the potassium iodide system. Reaction with a 50cm^3 volume produced a similar order of efficiency for the three reaction vessels (see Table. 3.24).

Table. 3.23 -Effect of reaction vessel changes on Fe^{3+}mol dm^{-3} on sonication of solution with a small sonic bath.

	REACTION VESSEL		
Time (mins)	**100cm^3 Conical Flask**	**250cm^3 Conical Flask**	**100cm^3 Round Bottomed Flask**
5	2.43x10^{-5}	1.62x10^{-5}	2.02x10^{-5}
10	4.46x10^{-5}	4.05x10^{-5}	3.65x10^{-5}
15	7.28x10^{-5}	6.47x10^{-5}	5.27x10^{-5}
30	13.40x10^{-5}	13.80x10^{-5}	9.71x10^{-5}
45	19.40x10^{-5}	19.40x10^{-5}	13.80x10^{-5}
60	23.90x10^{-5}	25.10x10^{-5}	17.40x10^{-5}

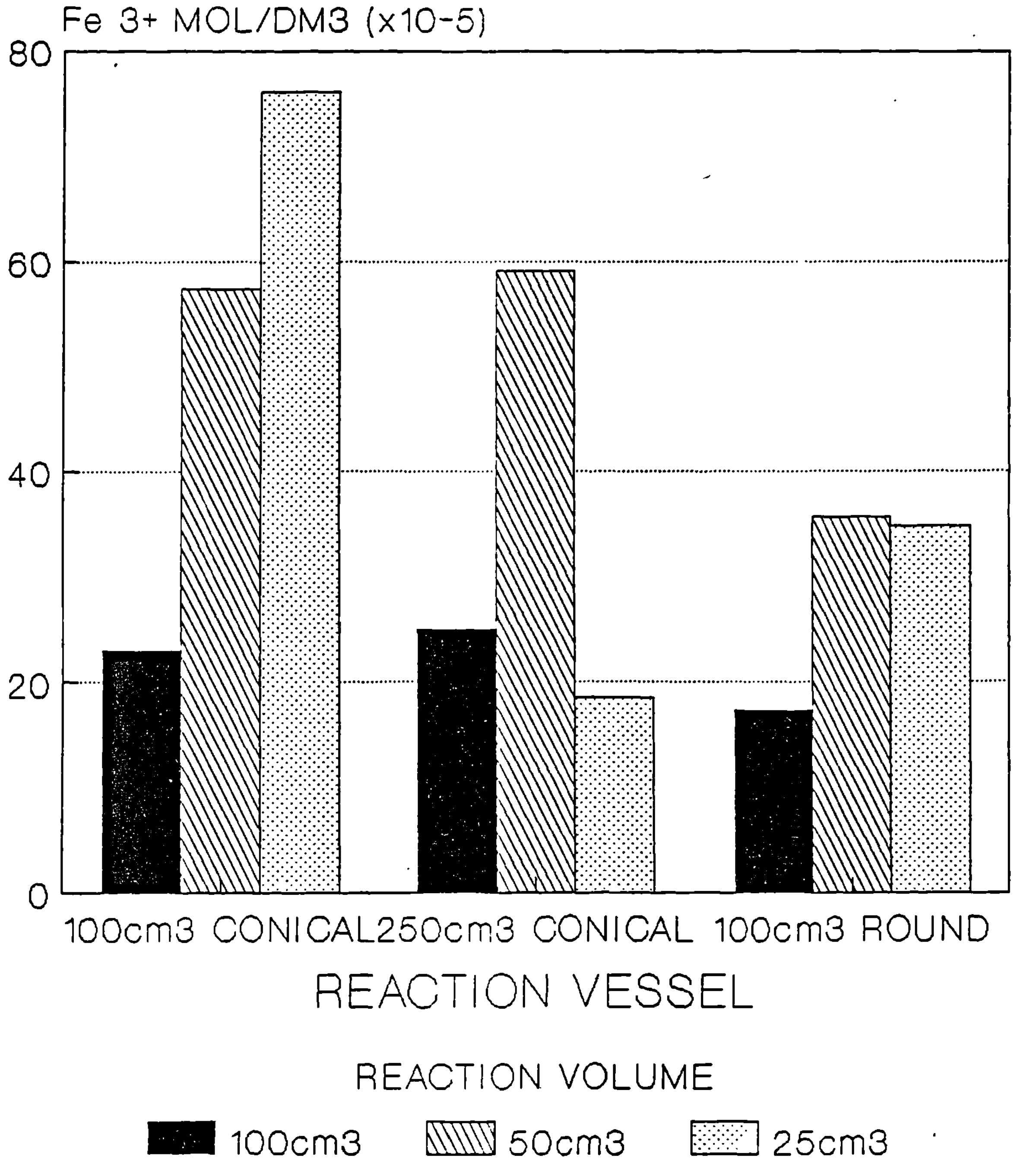
For 100cm^3 reaction volume, Fe^{2+}/ acid/ aerated.

Table. 3.24 -Effect of reaction vessel changes on Fe^{3+}mol dm^{-3} on sonication of with a small sonic bath.

	REACTION VESSEL		
Time (mins)	**100cm^3 Conical Flask**	**250cm^3 Conical Flask**	**100cm^3 Round Bottomed Flask**
5	8.09x10^{-5}	6.07x10^{-5}	6.47x10^{-5}
10	10.52x10^{-5}	8.90x10^{-5}	9.71x10^{-5}
15	15.77x10^{-5}	15.40x10^{-5}	12.14x10^{-5}
30	28.60x10^{-5}	25.50x10^{-5}	20.23x10^{-5}
45	42.10x10^{-5}	42.10x10^{-5}	27.50x10^{-5}
60	57.50x10^{-5}	59.13x10^{-5}	35.68x10^{-5}

For 50cm^3 reaction volume, Fe^{2+}/ acid/ aerated.

Fig 3.11 - Effect of reaction vessel changes on Ferric ion concentration on sonication with a small sonic bath



FRICKE DOSIMETER/ 60 MINS

For the 25cm^3 reaction volume however the trend observed is slightly different with the 250cm^3 conical flask producing the lowest amount of ferric ion, only 18.61x10^{-5}mol dm^{-3} when compared with 76.14x10^{-5} and 34.84^{-5}mol dm^{-3} for the 100cm^3 conical and round bottomed flasks respectively (see Table. 3.25 and Fig. 3.11). This is consistent with the results obtained using the potassium iodide dosimeter. The results for both dosimeters using a 25cm^3 reaction volume were also similar lending weight to the explanation offered previously (see section 3.6.1.1).

Table. 3.25 -Effect of reaction vessel changes on Fe^{3+}mol dm^{-3} on sonication with a small sonic bath.

	REACTION VESSEL		
Time (mins)	**100cm^3 Conical Flask**	**250cm^3 Conical Flask**	**100cm^3 Round Bottomed Flask**
5	4.05x10^{-5}	3.24x10^{-5}	4.05x10^{-5}
10	8.90x10^{-5}	4.05x10^{-5}	6.47x10^{-5}
15	13.76x10^{-5}	6.47x10^{-5}	8.90x10^{-5}
30	31.56x10^{-5}	12.14x10^{-5}	16.99x10^{-5}
45	49.38x10^{-5}	15.37x10^{-5}	24.27x10^{-5}
60	76.14x10^{-5}	18.61x10^{-5}	34.85x10^{-5}

For 25cm^3 reaction volume, Fe^{2+}/ acid/ aerated.

Reaction with the tube reactor and the push-pull reactor was not attempted because the absorption intensity of the ferric ion is low when compared to iodine and these systems do not provide enough sonic power. The detection limits were approached when sonicating a 50cm^3 solution employing the 0.6cm tip horn as no ferric ion could be detected for the first 15 minutes. As low values were obtained for a 25cm^3 solution sonication of a 50cm^3 solution with a 0.3cm tip horn was not attempted. The Fricke dosimeter is not as sensitive as the potassium iodide dosimeter. It was therefore thought that any ferric ion produced by this equipment would be too low for complete detection due to the large volumes employed.

3.6.2.3 Volume Alterations

As stated earlier an increase in reaction volume using the same energy source will result in an apparent decrease in yield of a sonochemical reaction and therefore the amount of ferric ion detected should fall with volume increase. For the probe system at setting 4 (10% output) volumes of 25cm^3, 50cm^3 and 100cm^3 reaction volumes result in 22.66x10^{-5}, 10.10x10^{-5} and 6.47x10^{-5}mol dm^{-3} of ferric ion respectively (see Table. 3.26 and Fig. 3.10).

Table. 3.26 -Effect of reaction volume changes on Fe^{3+}mol dm^{-3} on sonication with a 1.2cm diameter tip sonic probe.

Time (mins)	25 cm^3	50 cm^3	100 cm^3
5	7.28x10^{-5}	4.05x10^{-5}	3.24x10^{-5}
10	9.71x10^{-5}	6.08x10^{-5}	3.24x10^{-5}
15	12.14x10^{-5}	8.09x10^{-5}	3.65x10^{-5}
30	16.18x10^{-5}	10.93x10^{-5}	4.86x10^{-5}
45	19.42x10^{-5}	10.94x10^{-5}	6.47x10^{-5}
60	22.66x10^{-5}	10.10x10^{-5}	6.47x10^{-5}

Sonics and Materials Equipment, Setting 4, Power Output 10%.

For the sonic bath the vessel efficiencies are 100cm^3 conical> 100cm^3 round bottomed> 250cm^3 conical flask for a 25cm^3 reaction volume. For 50cm^3 and 100cm^3

reaction volumes the order was 250cm^3 conical > 100cm^3 conical > 100cm^3 round bottomed flask. These results also parallel those obtained using the potassium iodide dosimeter (see Tables. 3.27 to 3.29).

Table. 3.27 -Effect of reaction volume changes on Fe^{3+}mol dm^{-3} on sonication with a small sonic bath.

	100cm^3 CONICAL FLASK		
Time (mins)	**25 cm^3**	**50 cm^3**	**100 cm^3**
5	4.05x10^{-5}	8.09x10^{-5}	2.30x10^{-5}
10	8.90x10^{-5}	10.52x10^{-5}	4.46x10^{-5}
15	13.76x10^{-5}	15.77x10^{-5}	7.28x10^{-5}
30	31.56x10^{-5}	28.60x10^{-5}	13.40x10^{-5}
45	49.38x10^{-5}	42.10x10^{-5}	19.40x10^{-5}
60	76.14x10^{-5}	57.50x10^{-5}	23.85x10^{-5}

Table. 3.28 -Effect of reaction volume changes on Fe^{3+}mol dm^{-3} on sonication with a small sonic bath.

	250cm^3 CONICAL FLASK		
Time (mins)	**25 cm^3**	**50 cm^3**	**100 cm^3**
5	3.24x10^{-5}	6.07x10^{-5}	1.62x10^{-5}
10	4.05x10^{-5}	8.90x10^{-5}	4.05x10^{-5}
15	6.47x10^{-5}	15.40x10^{-5}	6.47x10^{-5}
30	12.14x10^{-5}	25.50x10^{-5}	13.80x10^{-5}
45	15.37x10^{-5}	42.10x10^{-5}	19.40x10^{-5}
60	18.61x10^{-5}	59.13x10^{-5}	25.10x10^{-5}

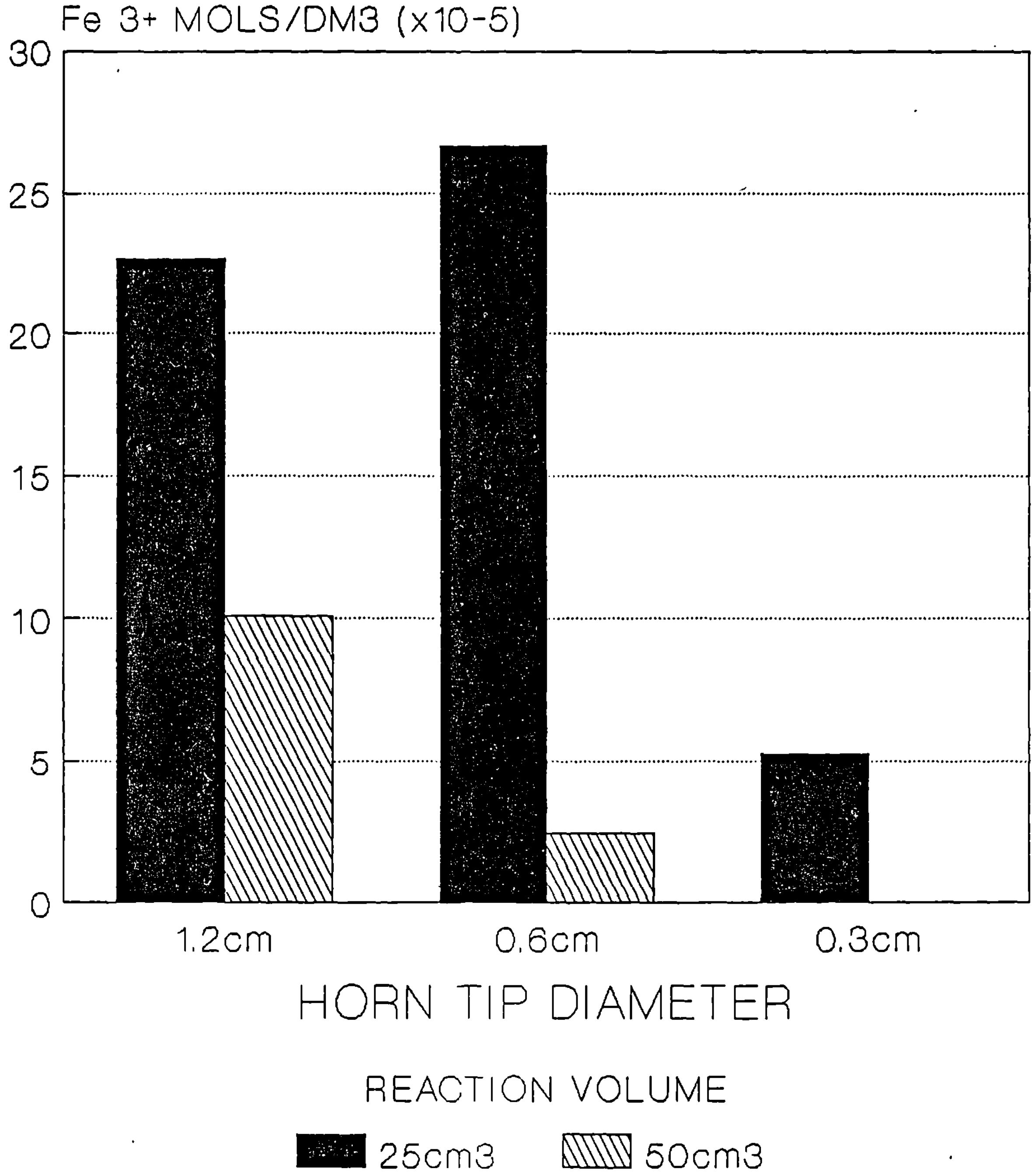
Table. 3.29 -Effect of reaction volume changes on Fe^{3+}mol dm^{-3} on sonication of with a small sonic bath.

	100cm^3 ROUND BOTTOMED FLASK		
Time (mins)	**25 cm^3**	**50 cm^3**	**100 cm^3**
5	4.05x10^{-5}	6.47x10^{-5}	2.02x10^{-5}
10	6.47x10^{-5}	9.71x10^{-5}	3.65x10^{-5}
15	8.90x10^{-5}	12.14x10^{-5}	5.27x10^{-5}
30	16.99x10^{-5}	20.23x10^{-5}	9.71x10^{-5}
45	24.27x10^{-5}	27.50x10^{-5}	13.80x10^{-5}
60	34.85x10^{-5}	35.68x10^{-5}	17.40x10^{-5}

3.6.2.4 Horn Alterations

As stated previously (see earlier Horn Alterations) the various horn tips emit different intensities of ultrasound. The 0.3cm diameter horn emits approximately 130W cm^{-2} but due to its narrow tip the actual field of sonication is smaller than that obtained with a 1.2cm diameter horn which only emits 30W cm^{-2} intensity of sonication. For a 25cm^3 reaction volume the horn which produced the most efficient reaction was the 0.6cm diameter tip (area of 0.28cm^2). The 1.2cm diameter tip (area of 1.13cm^2) was the next efficient with the 0.3cm diameter tip (area 0.071cm^2) the least efficient. The poor performance of the horn with 1.2cm tip was almost certainly due to the fact that the 25cm^3 reaction volume was unable to sustain the intensity of cavitation produced. The solution 'decouples' from the horn and a reduced yield of ferric ion results (see Table. 3.30 and Fig. 3.12).

Fig 3.12 - **Effect of horn alterations on Ferric ion concentration**



FRICKE DOSIMETER/ 60 MINS

Table. 3.30 - Effect of horn alterations on Fe^{3+}mol dm^{-3} on sonication with a sonic probe.

	HORN TIP DIAMETER				
	1.2 cm	1.2 cm	0.6 cm	0.6 cm	0.3 cm
Time (mins)	25cm^3	50cm^3	25cm^3	50cm^3	25cm^3
5	7.28x10^{-5}	4.05x10^{-5}	2.02x10^{-5}	-	3.24x10^{-5}
10	9.71x10^{-5}	6.08x10^{-5}	4.05x10^{-5}	-	5.27x10^{-5}
15	12.14 "	8.09x10^{-5}	6.47x10^{-5}	-	5.27x10^{-5}
30	16.18 "	10.93 "	11.33 "	0.81x10^{-5}	7.82x10^{-5}
45	19.42 "	10.94 "	17.80 "	2.02x10^{-5}	5.27x10^{-5}
60	22.66 "	10.10 "	26.70 "	2.43x10^{-5}	-

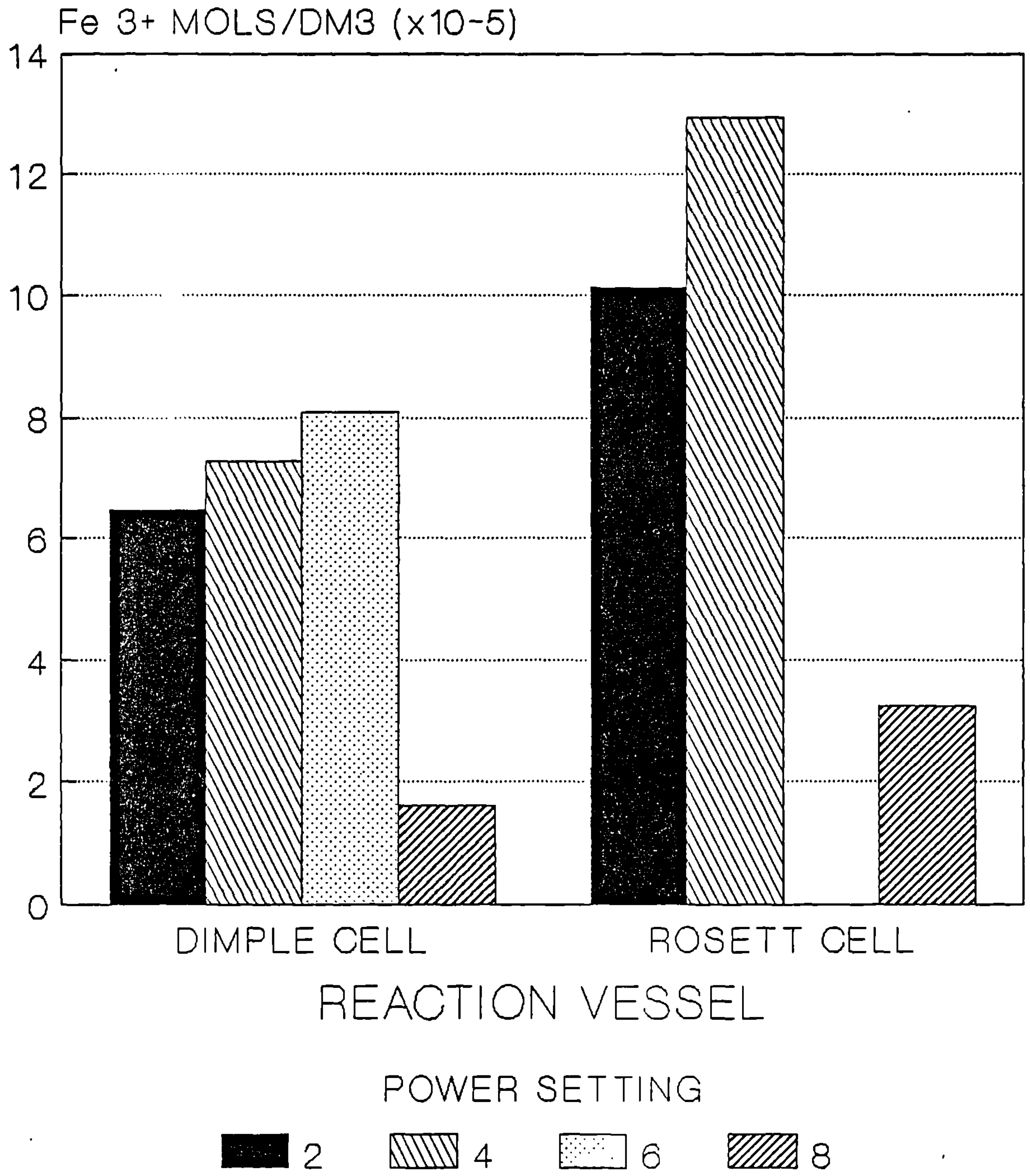
25cm^3 reaction volume, Fe^{2+}/ acid/ aerated, Power Output 9%/8%/7% depending upon the horn employed. Employing the Sonics and Materials generator.

When the reaction volume was increased to 50cm^3 the 1.2cm diameter probe produced the most efficient result followed by probe with the 0.6cm tip giving 10.10x10^{-5} and 2.43x10^{-5}mol dm^{-3} of ferric ion produced respectively, the larger reaction volume being capable of sustaining efficient cavitation produced by the larger tipped horns. The amount of cavitation produced by introducing a 0.3cm tip horn was not measured because the concentration of ferric ion was expected to be below the detection limit.

3.6.2.5 The Effect Of Power Alterations

As the power applied was increased the amount of ferric ion produced from 100cm^3 solution also increased. In the dimple cell, power settings of 2,4,6 and 8 generated concentrations of 6.47x10^{-5}, 7.28x10^{-5}, 8.09x10^{-5} and 1.62x10^{-5}mol dm^{-3} of ferric ion in 60 minutes respectively (see Table. 3.31 and Fig. 3.13). For the same volume and time

Fig 3.13 - Effect of applied power on Ferric ion concentration



FRICKE DOSIMETER/ 60 MINS

using the Rosett cell the power settings of 2,4,6 and 8 generated concentrations of 10.12×10^{-5}, 12.14×10^{-5}, 12.14×10^{-5} and 4.05×10^{-5}mol dm^{-3} of ferric ammonium sulphate (see Table. 3.32 and Fig. 3.13) showing the advantage of using a Rosett cell reactor.

Table. 3.31 - Effect of applied power on Fe^{3+}mol dm^{-3} on the sonicated oxidation of ferrous to ferric ions.

DIMPLE CELL				
Time (mins)	**Setting 2**	**Setting 4**	**Setting 6**	**Setting 8**
5	-	-	1.62×10^{-5}	-
10	1.62×10^{-5}	3.23×10^{-5}	3.65×10^{-5}	-
15	2.03×10^{-5}	2.84×10^{-5}	4.05×10^{-5}	0.49×10^{-5}
30	5.27×10^{-5}	4.05×10^{-5}	5.66×10^{-5}	1.62×10^{-5}
45	7.28×10^{-5}	6.47×10^{-5}	5.66×10^{-5}	2.02×10^{-5}
60	6.47×10^{-5}	7.28×10^{-5}	8.09×10^{-5}	1.62×10^{-5}

For 100cm^3 reaction volume, Fe^{3+}/ acid/ aerated. Sonicated with a 1.2cm diameter tip probe.

Table. 3.32 - Effect of applied power on Fe^{3+}mol dm^{-3} on the sonicated oxidation of ferrous to ferric ions.

ROSETT CELL				
Time (mins)	**Setting 2**	**Setting 4**	**Setting 6**	**Setting 8**
5	1.62×10^{-5}	1.62×10^{-5}	2.43×10^{-5}	2.43×10^{-5}
10	2.43×10^{-5}	4.05×10^{-5}	5.66×10^{-5}	4.05×10^{-5}
15	4.05×10^{-5}	5.66×10^{-5}	7.28×10^{-5}	4.85×10^{-5}
30	10.12×10^{-5}	9.71×10^{-5}	8.09×10^{-5}	4.85×10^{-5}
45	10.12×10^{-5}	12.14×10^{-5}	12.14×10^{-5}	4.05×10^{-5}
60	10.12×10^{-5}	12.95×10^{-5}	-	3.24×10^{-5}

For 100cm^3 reaction volume, Fe^{2+}/ acid/ aerated. Sonicated with a 1.2cm diameter tip probe. Sonics and Materials Generator.

In both vessels anomalous low results were obtained at the highest power setting. The power setting 8 is thought to produce such a high intensity level of sonication that the solution is unable to couple efficiently with it, resulting in a reduced amount of ferric ammonium sulphate being produced. This is an important consideration when attempting to increase sonochemical activity by power adjustment.

3.6.3 CALORIMETRY

3.6.3.1 The Effect Of Reaction Vessel Geometry

Sonic Probe

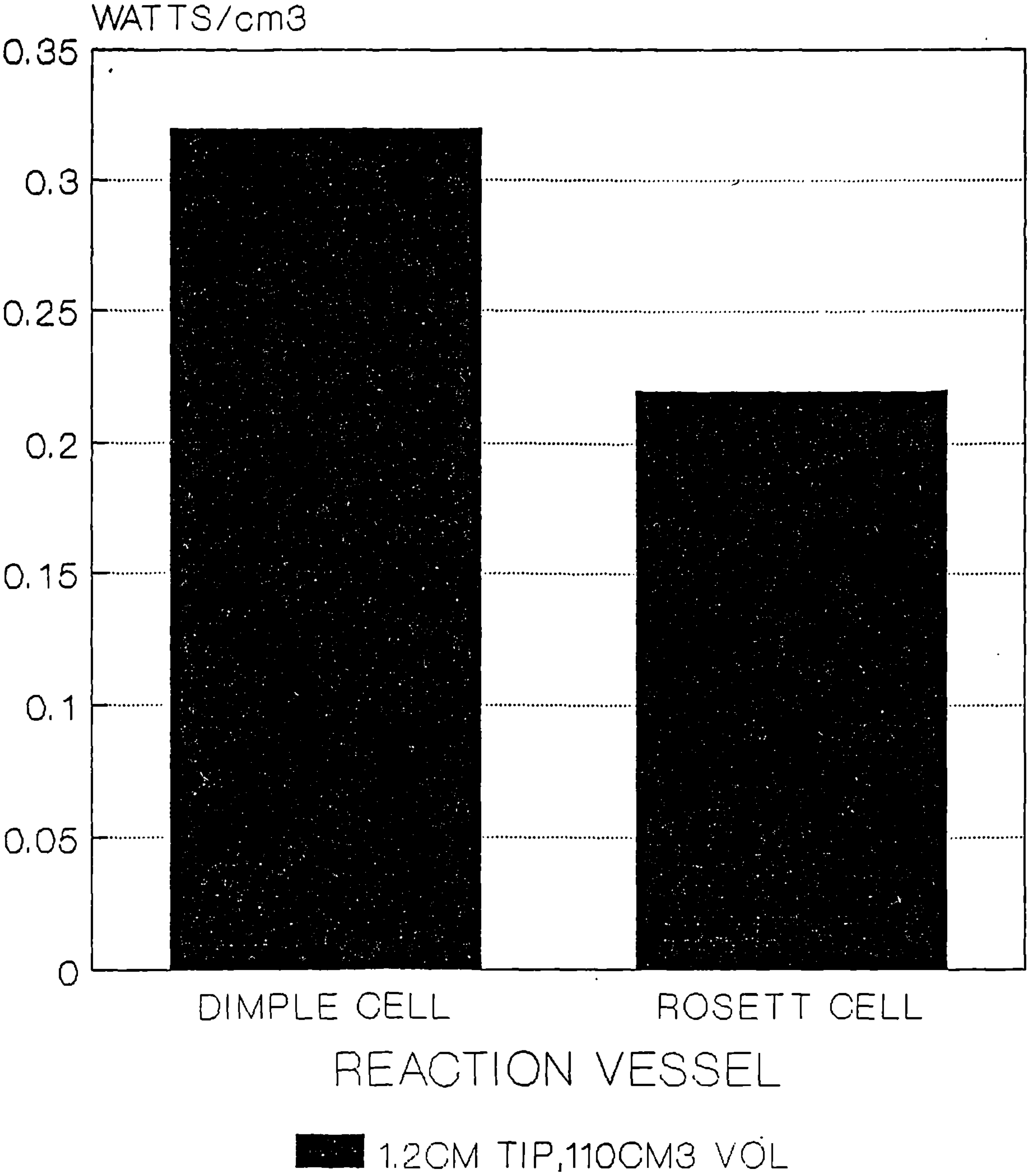
The power entering the Rosett cell appears to be significantly less than that entering the dimple cell although similar probe systems were employed (see Table. 3.33 and Fig. 3.14). This difference is certainly anomalous as it is important to note that while calorimetry would appear to suggest that more energy enters the dimple cell both chemical dosimeters suggest that the Rosette cell is more efficient.

Table. 3.33 - Comparison of Calorimetric results for dimple and Rosett cells.

	DIMPLE CELL	ROSETT CELL
Watts	35.66	24.07
Watts cm^{-2}	31.53	21.28
Watts cm^{-3}	0.32	0.22

For 1.2cm diameter tip and $110cm^3$ reaction volume.

Fig 3.14 - Effect of reaction vessel changes on the calorimetric result obtained on sonication with a sonic probe



Ultrasonic Bath

For a $110cm^3$ reaction volume a similar calorimetric result was obtained for all the reaction vessels employed approximately 25W (see Table. 3.34 and Fig. 3.15). This agreed with the results obtained with the chemical dosimeters (note the capacity of $100cm^3$ flasks is sufficient to hold $110cm^3$ solvent).

Table. 3.34 - Comparison of Calorimetric results for a $110cm^3$ reaction volume in a small sonic bath.

	REACTION VESSEL		
	$100cm^3$ CONICAL FLASK	**$250cm^3$ CONICAL FLASK**	**$100cm^3$ ROUND FLASK**
Watts	21.58	25.90	25.28
Watts cm^{-2}	5.47	0.41	-
Watts cm^{-3}	1.91	0.24	0.22

Area was difficult to determine for the round bottomed flask therefore power intensities per surface area were not determined.

Calorimetric measurements using $55cm^3$ reaction volume provided an anomalous result compared to that obtained by the other techniques. The chemical dosimeters both agreed that the $250cm^3$ reaction vessel provided the best reaction yields, probably due to the levels of solvent in the vessel, see earlier. The calorimetric result however suggests that it is the round bottomed flask which delivers the most power (see Table. 3.35 and Fig. 3.15). This may be due to some sort of focusing of the sonic waves by the round bottomed flask which provides heating rather than cavitation.

Fig 3.15 - Effect of reaction vessel changes on the calorimetric result obtained on sonication with a small sonic bath

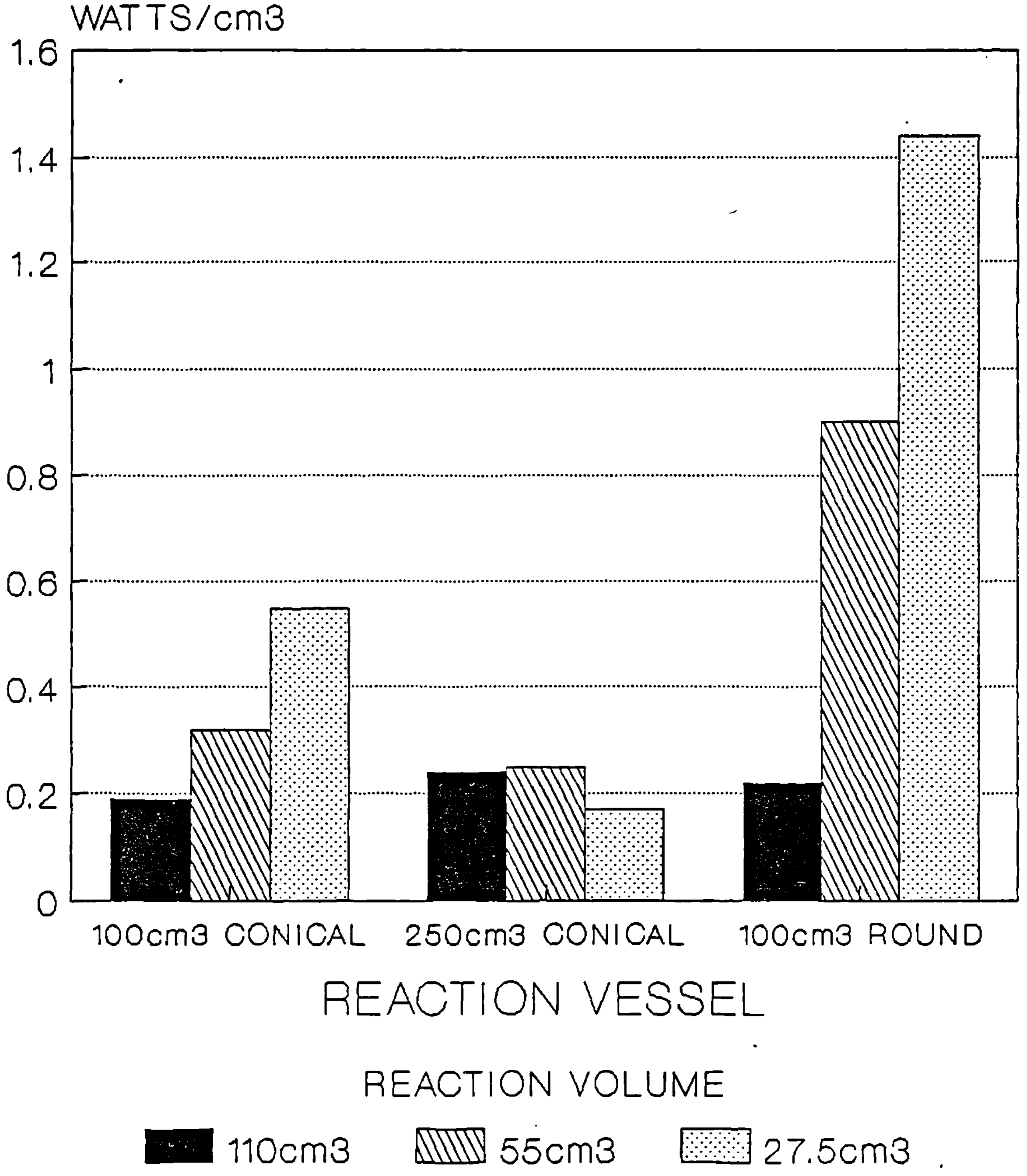


Table. 3.35 - Comparison of Calorimetric results for a 55cm^3 reaction volume in a small sonic bath.

	REACTION VESSEL		
	100cm^3 CONICAL FLASK	250cm^3 CONICAL FLASK	100cm^3 ROUND FLASK
Watts	17.40	13.96	49.58
Watts cm^{-2}	0.45	0.22	-
Watts cm^{-3}	0.32	0.25	0.90

Area was difficult to determine for the round bottomed flask therefore power intensities per surface area were not determined.

The 27.5cm^3 reaction volume (see Table. 3.36 and Fig. 3.15) produced identical results to those obtained by means of chemical dosimetry. The round bottomed flask provided by far the best calorimetric result (39.5W) and the 250cm^3 conical flask by far the worst (4.7W) suggesting inefficient coupling of the sound energy with the solvent medium.

Table. 3.36 - Comparison of Calorimetric results for a 27.5cm^3 reaction volume in a small sonic bath.

	REACTION VESSEL		
	100cm^3 CONICAL FLASK	250cm^3 CONICAL FLASK	100cm^3 ROUND FLASK
Watts	15.10	4.70	39.51
Watts cm^{-2}	0.39	0.07	-
Watts cm^{-3}	0.55	0.17	1.44

Area was difficult to determine for the round bottomed flask therefore power intensities per surface area were not determined.

Tube Reactor

From the calorimetric results (see Table. 3.37 and Fig. 3.16) there seemed to be an increase in sonic power with increasing tube volume. In each case of course there was an identical source of energy (the transducers on the pentagonal tube) but as the dimensions of the glass tubes were changed different amounts of energy were observed. As this was a homogeneous system a more uniform result was obtained with calorimetry.

Table. 3.37 - Comparison of Calorimetric results for the stationary Tube Reactor.

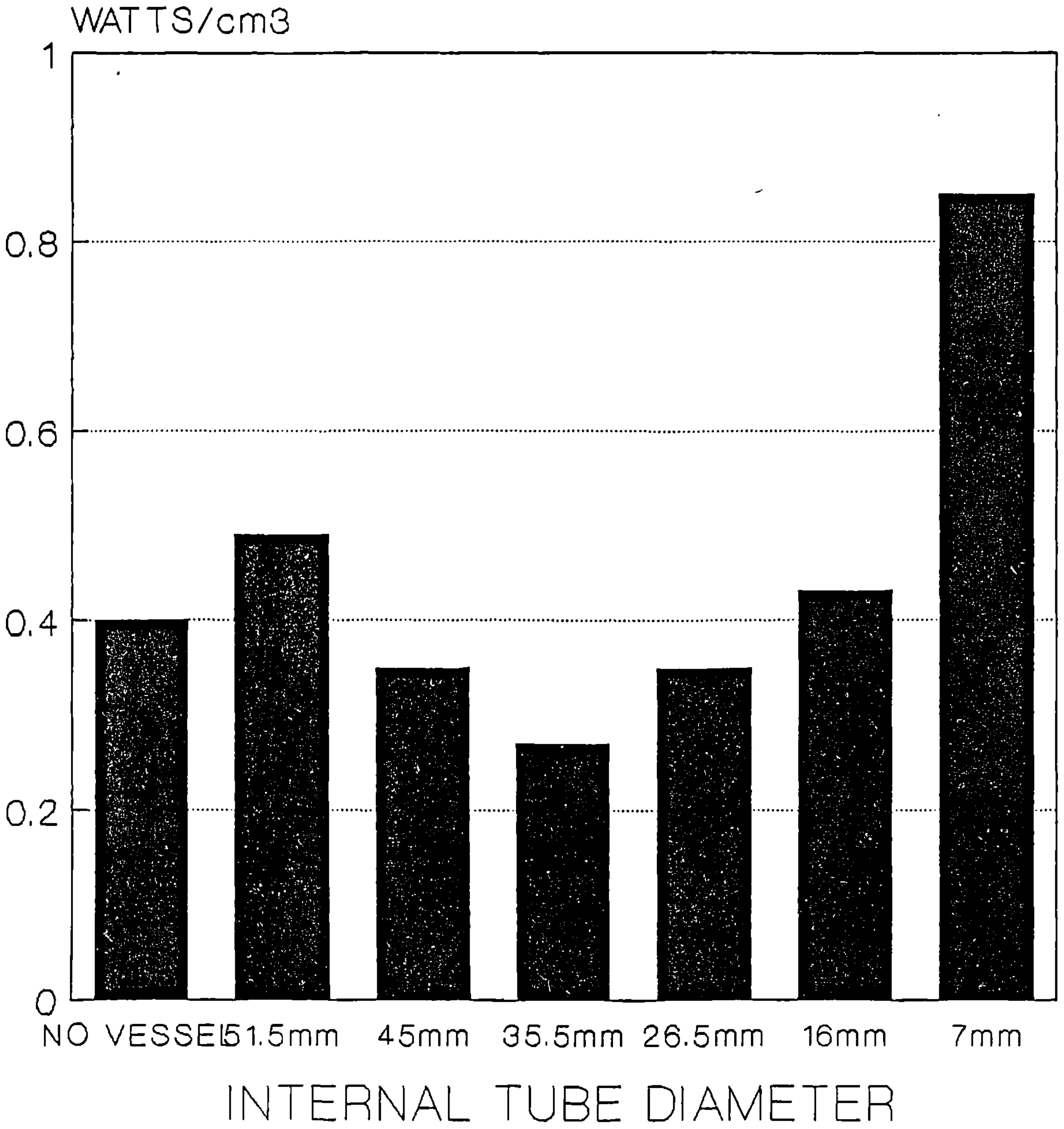
Tube Diameter	**Reaction Volume**	**Tube Area (Surface)**	**Watts**	**Watts cm^{-2}**	**Watts cm^{-3}**
No Tube*	1713.0cm^3	804.25cm^2	687.55	0.85	0.40
51.5mm	742.5cm^3	517.73cm^2	365.93	0.71	0.49
45.0mm	517.0cm^3	452.39cm^2	181.56	0.40	0.35
35.5mm	330.0cm^3	356.88cm^2	89.56	0.25	0.27
26.5mm	187.0cm^3	266.41cm^2	65.75	0.25	0.35
16.0mm	71.5cm^3	160.85cm^2	30.45	0.19	0.43
7.0mm	13.2cm^3	70.37cm^2	11.28	0.16	0.85

* No tube reactor vessel employed the actual diameter of the tube reactor is 70mm.

Problems were encountered with the chemical dosimeters. Due to the lack of emulsification of carbon tetrachloride the potassium iodide dosimeter gave an unusual result (see earlier 3.6.1.1) and the homogeneous ferric ion dosimeter was not attempted due to the low levels of power emitted by the tube reactor.

Thermal calorimetry was not attempted on flow systems because the movement of the

Fig 3.16 - Effect of reaction vessel changes on the calorimetric result obtained on sonication with the tube reactor



solvent would disrupt readings.

3.6.3.2 Volume Alterations

Ultrasonic Probe

The calorimetric results (see Table. 3.38) indicated that this technique provides a useful measure of power output. For all three reaction volumes studied a similar power (and intensity) of ultrasound entered the system, 45W and 39Wcm^{-2} respectively. This would be expected to be the case because the same probe system and power setting was employed for all experiments. However the sonication power per unit volume must necessarily change as the reaction volume increases giving a lower dosimetric response with the larger reaction volumes.

Table. 3.38 - Comparison of Calorimetric results for a 1.2cm diameter sonic probe.

	REACTION VOLUME		
	27.5cm^3	**55cm^3**	**110cm^3**
Watts	45.15	42.89	48.50
Watts cm^{-2}	39.94	37.48	42.87
Watts cm^{-3}	1.64	0.78	0.44

Ultrasonic Bath

In the 100cm^3 conical flask there appeared to be similar levels of ultrasound entering the 27.5cm^3 and 55cm^3 reaction volumes (see Table. 3.39 and Fig. 3.15). The 110cm^3 reaction volume may undergo some sort of 'focusing' effect as the calorimetric result was much higher than expected, 21W compared with approximately 16W for the others. This anomalous 'focusing effect' seems to relate only to heat generation however because it is not reflected in the chemical dosimeter responses.

Table. 3.39 - Comparison of Calorimetric results for a 100cm^3 Conical flask sonicated by a small sonic bath.

	REACTION VOLUME		
	27.5cm^3	**55cm^3**	**110cm^3**
Watts	15.10	17.39	21.58
Watts cm^{-2}	0.39	0.45	0.56
Watts cm^{-3}	0.55	0.32	0.19

The 250cm^3 conical flask appeared to give better calorimetric results (4.7W, 13.9W and 25.9W) as the reaction volume increased from 27.5, 55 to 110cm^3 (see Table. 3.40). This may indicate a better coupling of the ultrasound to the solvent as the volumes increases. This is in accord with the poor chemical dosimeter response observed for the 27.5cm^3 reaction volume.

Table. 3.40 - Comparison of Calorimetric results for a 250cm^3 Conical flask sonicated by a small sonic bath.

	REACTION VOLUME		
	27.5cm^3	**55cm^3**	**110cm^3**
Watts	4.70	13.96	25.90
Watts cm^{-2}	0.07	0.21	0.41
Watts cm^{-3}	0.17	0.25	0.24

The 100cm^3 round bottomed flask provided the best calorimetric result with a 55cm^3

reaction volume (see Table. 3.41). However chemical dosimetry produced the best result with the 250cm^3 conical flask (see earlier) this was thought to be due to the depth of the solvent within the conical flask resembling a quarter wavelength of 38kHz sonic waves in water. There is clearly some difference in the monitoring of temperature rise and radical formation as estimates for sonochemical efficiency.

Table. 3.41 - Comparison of Calorimetric results for a 100cm^3 Round Bottomed flask sonicated by a small sonic bath.

	REACTION VOLUME		
	27.5cm^3	**55cm^3**	**110cm^3**
Watts	39.51	49.57	25.28
Watts cm^{-3}	1.44	0.90	0.23

3.6.3.3 Horn Alterations

At the same generator setting, and 27.5cm^3 reaction volume, the amount of power entering the reaction system fell as the tip diameter decreased from 27.8W for the 1.2cm diameter tip to 10W for the 0.3cm diameter tip (see Table. 3.42 and Fig. 3.17). It should be noted however that under these circumstances the power intensity at the probe tip (W cm^{-2}) increases as the tip size is reduced. Thus for the 1.2cm tip (area 1.13cm^2) the power intensity is 24.6W cm^{-2} whereas for the 0.3cm tip (area 0.071cm^2) the intensity is 141.7W cm^{-2}.

Fig 3.17 - Effect of horn alterations on the calorimetric results obtained

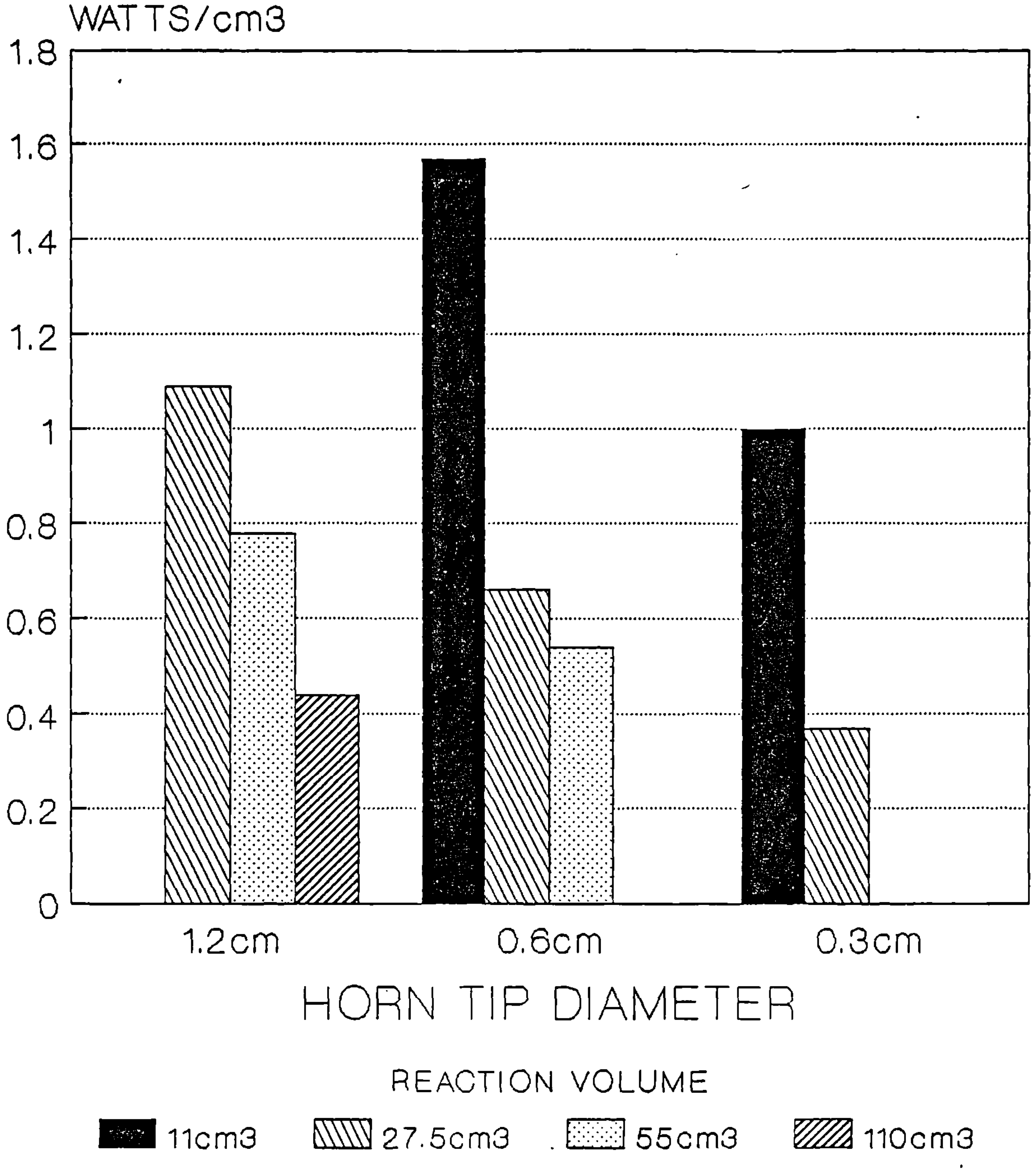


Table. 3.42 - Comparison of Calorimetric results for a sonic probe 27.5cm^3 reaction volume.

	HORN DIAMETER		
	1.2 cm	**0.6 cm**	**0.3 cm**
Watts	27.76	18.03	10.06
Watts cm^{-2}	24.55	63.73	141.68
Watts cm^{-3}	1.09	0.66	0.37

Table. 3.43 - Comparison of Calorimetric results for a 0.3cm diameter probe tip.

	REACTION VOLUME	
	11.0 cm^3	**27.5 cm^3**
Watts	11.05	10.06
Watts cm^{-2}	155.29	141.68
Watts cm^{-3}	1.00	0.37

Table. 3.44 - Comparison of Calorimetric results for a 0.6cm diameter probe tip.

	REACTION VOLUME		
	11.0 cm^3	**27.5 cm^3**	**55.0 cm^3**
Watts	17.26	18.03	29.91
Watts cm^{-2}	60.99	63.73	84.40
Watts cm^{-3}	1.57	0.66	0.54

3.6.3.4 Power Alterations

Calorimetric results indicated that as the probe settings for the 1.2cm tip were increased from 2 to 6 the power entering 110cm^3 also increased to give 40.3W, 55.6W and 78.4W respectively (see Table. 3.45 and Fig. 3.18).

Fig 3.18 - Effect of power alterations on the calorimetric results obtained for a sonic probe system

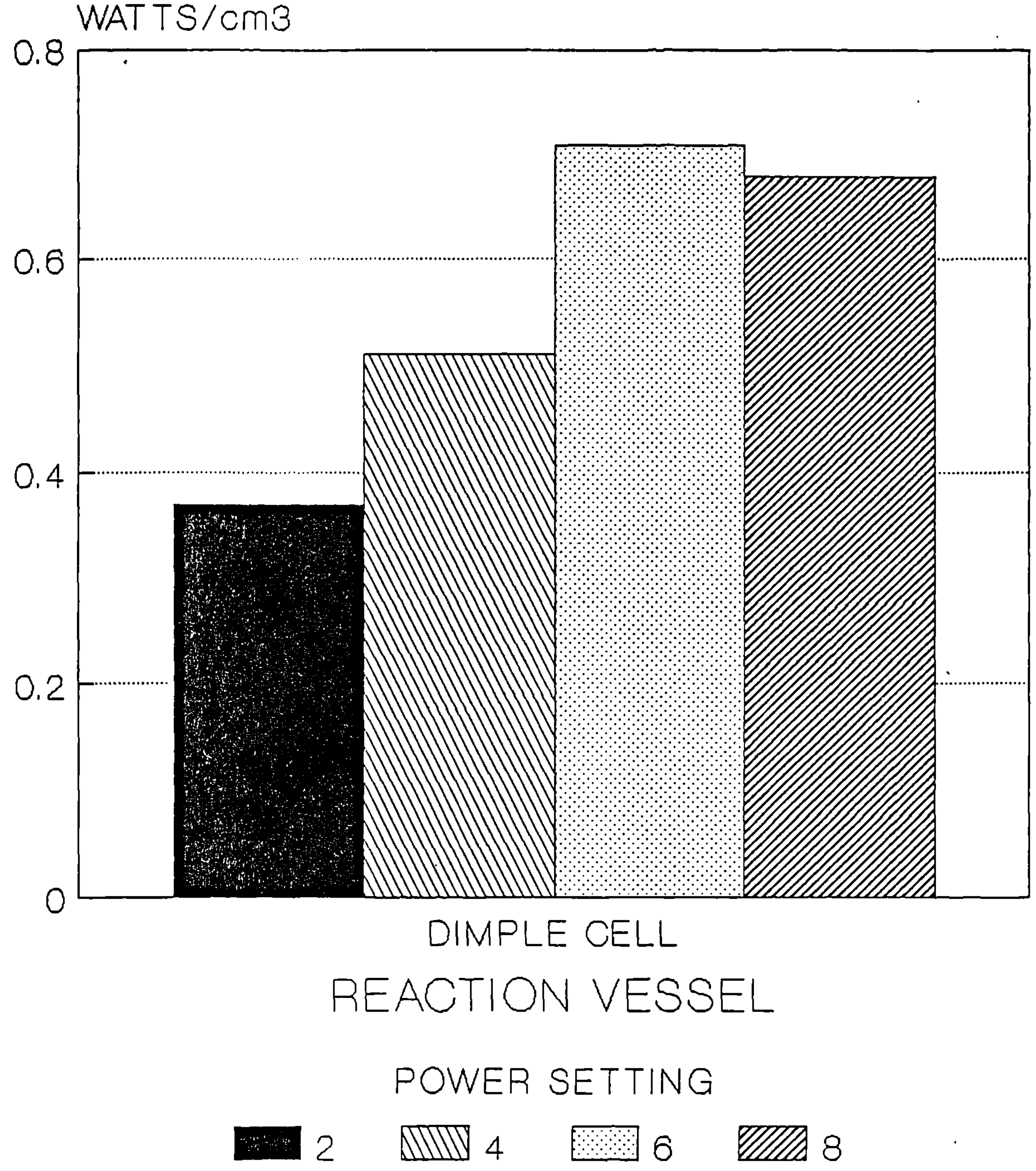


Table. 3.45 - Comparison of Calorimetric results for a dimple cell, employing a 1.2cm tip horn.

	POWER SETTING			
	2	**4**	**6**	**8**
Watts	40.27	55.58	78.35	74.60
Watts cm^{-2}	35.60	49.15	69.28	66.00
Watts cm^{-3}	0.37	0.51	0.71	0.68

This confirmed the chemical dosimetry results which showed that as the power applied was increased the reaction yield also increased. The result obtained at setting 8 showing a drop in reaction yield confirms the chemical dosimeter results and indicates some decoupling at high power.

3.6.3.5 The Effect Of Temperature Alterations

There appears to be a similar amount of power entering the reaction vessel at the different reaction temperatures using the same probe system (see Table. 3.46 and Fig. 3.19). This suggests that the probe does not lose efficiency as the temperature rises. The fact that the chemical dosimeters indicated that the yield of reaction decreased with rise in temperature suggests that sonochemical efficiency was reduced as a result of other factors *e.g.* more vapour entering the cavitation bubbles thus reducing the efficiency of cavitational collapse.

Fig 3.19 - Effect of reaction temperature alterations on the calorimetric results obtained for a sonic probe system

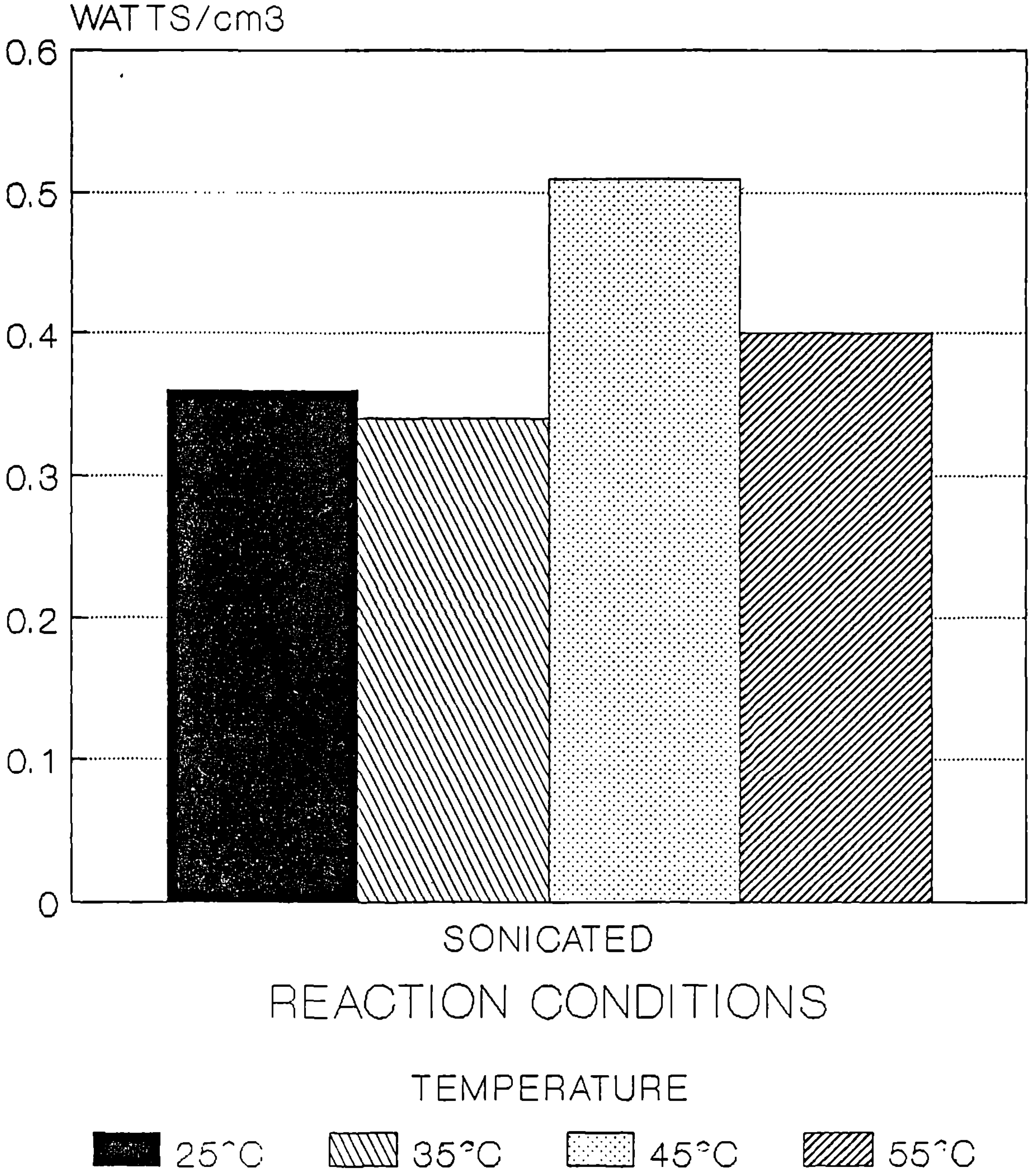


Table. 3.46 - Effect of temperature on the Calorimetric Results of a reaction sonicated with a 1.2cm diameter tip in a dimple cell.

	REACTION TEMPERATURE			
	25°C	35°C	45°C	55°C
Watts	39.67	36.93	55.95	43.86
Watts cm^{-2}	35.11	32.68	49.46	38.82
Watts cm^{-3}	0.36	0.34	0.51	0.40

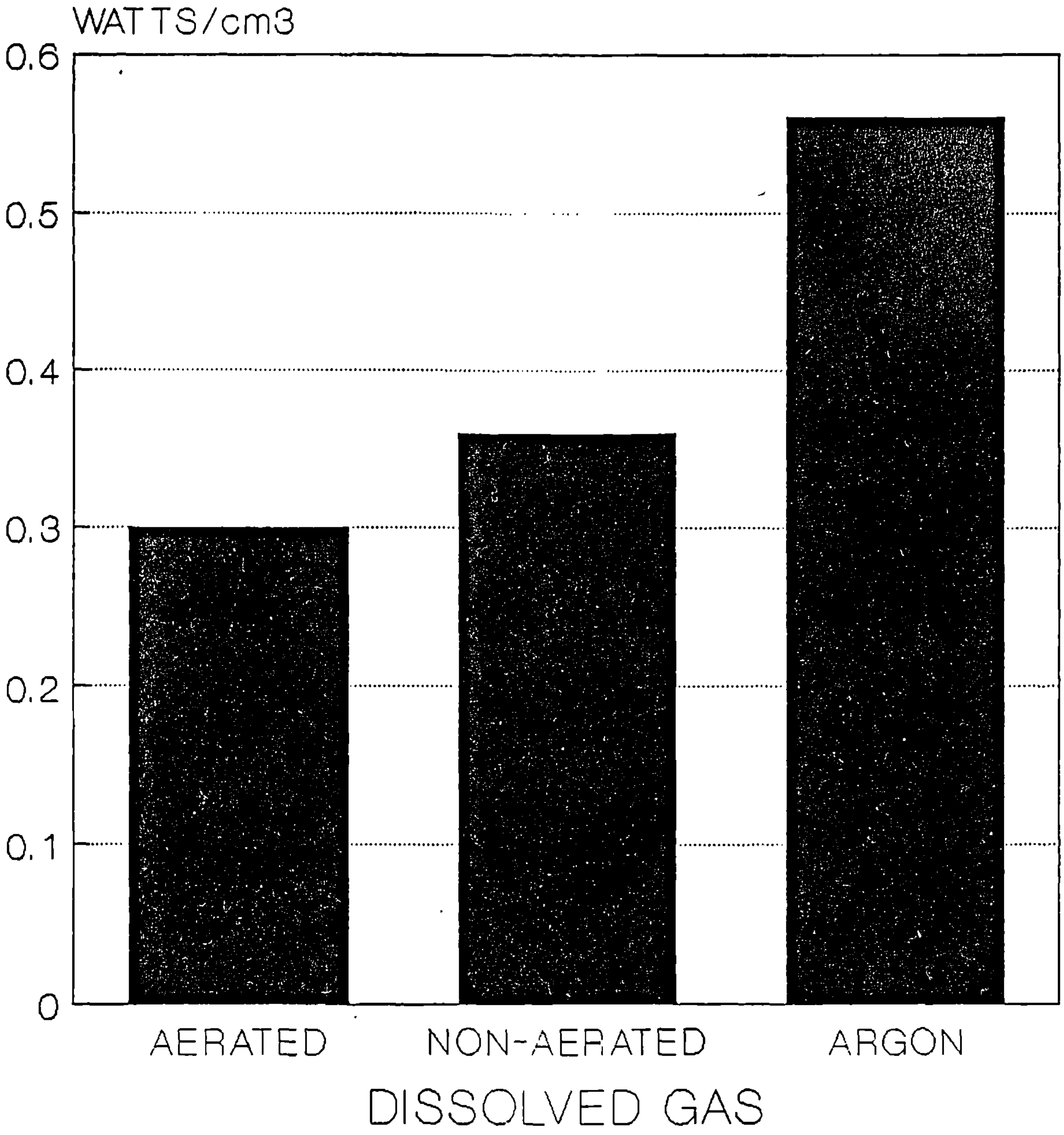
3.6.3.6 Effect of Dissolved Gases

Argon produced by far the most effective power dissipation into the reaction system being over twice as good as air (see Table. 3.47 and Fig. 3.20). This backed-up the chemical dosimetric results obtained which also showed argon to be most effective in providing reaction yield enhancement.

Table. 3.47 - The effect of introducing Argon into a sonicating system.

	Aerated	Non-Aerated	Argon
Watts	32.87	39.67	61.89
Watts cm^{-2}	29.09	35.11	54.77
Watts cm^{-3}	0.30	0.36	0.56

Fig 3.20 - Effect on the calorimetric result of introducing Argon into the sonicating system



3.6.4 Observation of changes in pH and UV absorbance for a series of solutions

A series of experiments were performed to investigate the factors which influence the increased production of iodine during the sonication of aqueous potassium iodide in the presence of carbon tetrachloride.

Samples of 25cm^3 volumes were sonicated using a probe with a 0.6cm tip employing the Sonics and Materials equipment at setting 4 (8% output). The solution pH was monitored before and after 5 minutes sonication.

Solution	Initial pH	Final pH	Conclusion
Distilled Water	4.21	4.21	No change in acidity
Water plus CCl_4	3.8	3.13	Slight formation of H^+
Aqueous KI	6.5	6.5	No change in acidity
Aqueous KI plus CCl_4	6.5	4.19	A large amount of H^+ formed *

In solutions where carbon tetrachloride was added a volume of 0.25cm^3 was introduced. In solutions where acid was required a volume of 2.5cm^3 of the respective 2M acid was added.

The drop in pH in the presence of carbon tetrachloride is probably due to the formation of HCl and hypohalous acid via the following reactions:-

$$CCl_4 + H_2O \rightarrow CO + Cl_2 + 2HCl$$

or

$$Cl_2 + H_2O \rightarrow HCl + HClO$$

A further series of experiments were attempted to investigate if the effect of acidity, via the formation of HCl generated by the sonication of aqueous carbon tetrachloride, influences the rate of iodine production. The UV spectra were obtained of the iodine solutions after the sonication of a series of samples.

Solution	UV Abs (350nm)	Conclusion
aq KI	0.043	Poor iodine production
aq KI/H_2SO_4	0.11	Addition of H_2SO_4 doubles iodine production
aq KI/HCl	0.103	Addition of HCl doubles iodine production.

From the results it is clear that lowering the pH of the solution does enhance iodine production but the actual acid added does not appear to be important.

Solution	UV Absorbance (350nm)	Conclusion
KI/CCl_4/No acid	0.249 (diluted by 10)	Addition of CCl_4 enhances iodine by a minimum factor of 20.
KI/CCl_4/H_2SO_4	0.27 (diluted by 10)	Similar iodine levels
KI/CCl_4/HCl does	0.214 (diluted by 10)	Similar yield to CCl_4/No acid. Acid not play a large part in iodine production once CCl_4 is added.

For aqueous KI the presence of H^+ ions does enhance the yield slightly (by a factor of 2). Addition of CCl_4 to aqueous KI enhances the yield greatly (by a factor of 20). In the presence of CCl_4 however the liberation of iodine from KI by sonication is little affected by the addition of acid.

Addition of trichloromethane

The replacement of carbon tetrachloride by trichloromethane enhances the sonochemical production of iodine, from aqueous potassium iodide (by a factor of 10). This enhancement is only half that observed with carbon tetrachloride.

Solution	UV Absorbance (350nm)	Conclusion
KI/ H^+	0.103	
KI/$CHCl_3$	0.10 (diluted by 10)	Iodine production enhanced by a factor of 10.
KI/$CHCl_3$/H^+	0.12 (diluted by 10)	Iodine production enhanced by a factor of 10.
HCl	0.002	HCl does not absorb at UV 350nm.

It is thought that the C-H bond would break preferentially to produce the slightly more 'stable' $CCl_3\cdot$ radicals and $H\cdot$ radicals rather than $Cl\cdot$ and $CHCl_2\cdot$ radicals.

$$CHCl_3 \rightarrow H\cdot + CCl_3\cdot$$

rather than

$$CHCl_3 \rightarrow Cl\cdot + CHCl_2\cdot$$

resulting in less $Cl\cdot$ radical recombination reaction.

For $CHCl_3$/ H_2O:-

$$H\cdot + HCCl_3 \rightarrow H_2 + CCl_3\cdot$$

$$H\cdot + HCCl_3 \rightarrow Cl\cdot + HCCl_2\cdot \text{ less likely step}$$

$$Cl\cdot + HCCl_3 \rightarrow HCl + CCl_3\cdot$$

Thus $Cl\cdot + Cl\cdot \rightarrow Cl_2$ less likely.

One route from which iodine may possibly be formed is via the oxidation of iodide by chlorine. This was investigated using chlorine generated by the addition of acid to sodium hypochlorite.

$$NaOCl + HCl \rightarrow HOCl + NaCl$$

$$HOCl + HCl \rightarrow Cl_2 + H_2O$$

On addition of HCl, via a dropping funnel, to a flask containing sodium hypochlorite the solution first assumes a yellow discolouration effervescence occurs and a green/ yellow gas, which bleaches damp litmus and turns KI paper black, is evolved. This gas passes from the flask through a Dreschel flask containing silicone oil to a second Dreschel flask where it can be collected. A glass pipette was used to transfer this gas into an aqueous potassium iodide solution. On addition of the chlorine gas to potassium iodide solution the characteristic metallic black of elemental iodine was instantaneously produced. This diffused into the clear solution turning it orange. UV analysis at 350nm indicated the presence of iodine.Chlorine oxidises iodide ions very effectively itself being reduced to Cl^- (note Cl_2 has a redox potential of 1.36 and I_2 has a redox potential of 0.5).

$$2I^- \rightarrow I_2^o + 2e^-$$

$$Cl_2^o + 2e^- \rightarrow 2Cl^-$$

Other oxidising agents such as HOCl are also thought to be present and may also contribute to iodine production. Much more work would be necessary to unravel the complex reactions occurring on the sonication of aqueous potassium iodide in the presence of carbon tetrachloride.

3.7 ERROR ESTIMATION

Factors which contribute to the average experimental error include volumetric deviations which are present in the initial preparation of the samples and are approximately ±0.25% of the individual volumes employed. As the samples are diluted further for analysis purposes dilution errors of approximately ±0.05% of the respective volumes are present. Ultrasonic equipment heats up with time and temperature deviations to a maximum of ±1.5% exist, depending upon the equipment employed and the length of time it is in operation. The maximum overall error present for the above work is approximately ±5% but variations from this value will occur for each individual experiment.

3.8 CONCLUSION

In general the 3 calibration methods investigated, namely the potassium iodide dosimeter, Fricke dosimeter and thermal calorimetry all produced similar trends with respect to equipment type and reaction vessel type.

The addition of carbon tetrachloride to aqueous potassium iodide reduces the reproducibility of this dosimeter but iodine production is increased and the sensitivity is increased. It is important to ensure that the emulsification of carbon tetrachloride on sonication is complete as this maximises iodine production and also improves reproducibility.

The Fricke dosimeter confirmed the results obtained by the potassium iodide dosimeter. This system is homogeneous so no emulsification problems occur. Unfortunately however the Fe^{3+} ion has a low ultraviolet/ visible extinction coefficient. This low UV response limits the effective use of the Fricke dosimeter to the more powerful ultrasonic sources with which a high chemical response would be expected.

Calorimetry is an efficient 'physical' method of determining sonication power by the direct measurement of the temperature rise within the reaction medium, but only if mixing of the solution is efficient and no overly 'hot' or 'cold' spots are present.

Generally for reaction volumes of about 100cm^3 the sonic probe is the best source of ultrasound. The 1.2cm diameter tip is the most efficient source of ultrasound followed by the 0.6 cm diameter tip. A Rosett cell appears to be the most efficient reaction vessel.

Next in the order of sonication efficiency for small volumes of 100cm^3 is the sonic bath as reactor. For smaller volumes the most efficient sonochemical response was obtained when employing a 100cm^3 round bottomed flask.

The 0.3cm diameter probe tip with its smaller tip area of sonication produces very high intensity sonication in a small active volume. It is best for very small volumes < 25cm^3.

For all systems care must be taken not to exceed an input power which exceeds the tolerance of the liquid reaction. Decoupling is a major source of reaction inefficiency.

The tube reactor, as a stationary bath is the least efficient source of sonication when employing small reaction volumes in glass tubes.

For large volumes it appears that the Push-Pull reactor (with 6.6 litre capacity) is certainly more efficient than the pentagonal tube reactor flow system (4 litre capacity).

The efficiency of sonication alters as such factors as sonication source, reaction volume and vessel type are altered. Reactions must be repeated under as similar conditions as possible for reproducibility and comparison. Reporting of results must also contain information to the exact reaction 'set up' in order for similar reactions to be attempted elsewhere.

Sonication of reactions introduces complex problems in which physical factors such as vessel geometry, power and temperature become very important.

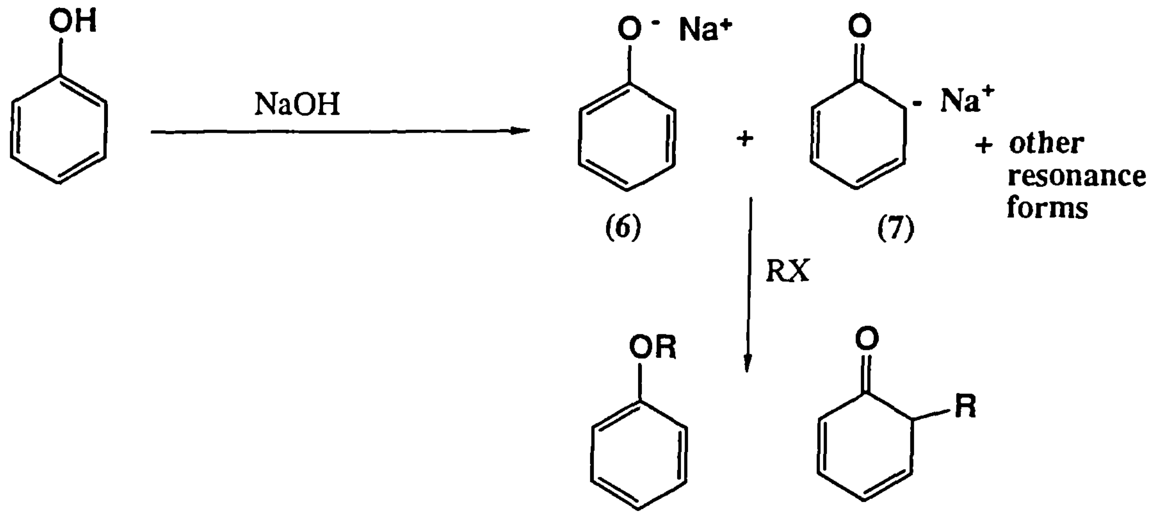
CHAPTER 4

SONOCHEMICALLY ASSISTED O-ALKYLATION OF PHENOLS

4.0 THE O-ALKYLATION OF PHENOLS

4.1 INTRODUCTION

The Williamson ether synthesis is a well known route to aromatic ethers. This is often achieved via electrophilic attack of an alkyl halide on the corresponding aromatic phenol in the presence of a base, such as potassium carbonate.



Electrophilic attack may occur at two positions, at the phenolic oxygen (6) or at a ring carbon (7). Many studies have been undertaken in an effort to determine an effective route to either exclusive O-alkylation or C-alkylation. The effect of solvent on the O/ C ratio of products has been closely studied.

Kornblum et al[46] noted that often alkylation of a phenoxide ion results in exclusive O-alkylation in most solvents. However if polar protic solvents, solvents which are able to form strong hydrogen bonds, are used then the route of reaction alters and almost exclusive C-alkylation occurs. This is thought to be due to more effective solvation of the 'localised' negative charge on the oxygen. This solvation provides an effective barrier to approaching alkyl cations. This results in alkylation preferably occurring at the α-ring carbons where solvation is not as effective. This argument may be taken further. C-alkylation is increased as oxygen solvation is increased. Increasing the orientation of a solvent around the oxygen ion via the application of pressure will increase C-alkylation simply because the solvent barrier around the oxygen ion will be more effective.

Le Noble[47] attempted this approach obtaining results indicating increased C-alkylation in water, an effective hydrogen bonding solvent. C-alkylation in methanol was also forced even though it is not an effective hydrogen bonding solvent and oxygen ion solvation is poor within this solvent.

Kornblum et al[48] also investigated the alkylation of sodium β-naphthoxide, which has a more evenly balanced O/C-alkylation ratio than the phenoxide ion. Sodium naphthoxide should be more susceptible to solvent influence on alkylation and reaction products may be altered as the solvent is changed from aprotic, no hydrogen bonding, to protic, hydrogen bonding. Alkylation in dimethyl formamide and dimethylsulphoxide, polar aprotic solvents, results in 97% O-alkylation to give the naphthyl ether. Alkylation in water, polar protic solvent, results in 84% C-alkylation and 10% O-alkylation. Unlike phenoxides the similar O/C ratio in naphthoxides results in differences even in aprotic solvents. For example 36% C-alkylation occurs in the aprotic tetrahydrofuran. This is thought to be due to the dielectric effect, the ability of the solvent to decrease electrostatic interactions.

Dimethylformamide and dimethylsulphoxide have high dielectric constants while tetrahydrofuran has a low dielectric constant. In low dielectric solvents sodium naphthoxide must exist as an associated ion pair. O-alkylation is hindered due to the strong attraction of the sodium for the concentrated charge on the oxygen, thus

C-alkylation now becomes a competitive reaction.

In high dielectric solvents free naphthoxide ions may exist, if the solution is dilute enough, and these will be highly reactive to O-alkylation. In concentrated solutions a dissociated ion pair will exist thus O-alkylation can still occur in preference to C-alkylation.

Another approach to the control of the alkylation site was attempted by Smith and Hanson[49]. If the site of alkylation is in part governed by the degree of dissociation of the salt then increasing or decreasing the amount of dissociation will increase or decrease the amount of O-alkylation.

Alkylation of sodium 9-fluorenone oximate with methyl iodide results in a decrease in rate as the concentration is increased, with O-alkylation also decreasing from 64% to 46%. This suggests that the dissociated ion is more reactive than the associated ion and the amount of O-alkylation is determined by the degree of association. Addition of dibenzo-18-crown-6-polyether promotes dissociation and results in a rate increase with 64% O-alkylation and 35% N-alkylation. Addition of sodium tetraphenylboride results in association of the species, a result of the increased amount of sodium ions in solution. The product composition indicates a complete reversal of the site of alkylation with 68% N-alkylation occurring. A rate decrease of a factor of 70, from that observed in the presence of crown ether, also occurs.

O-alkylation is preferred in polar aprotic solvents in which a high degree of ion dissociation is present, while C-alkylation prefers protic solvents and associated ions.

Enhancement of O-alkylation is thought to be in part due to an increase in base surface area. With heterogeneous reactions in mind many studies have been undertaken to determine the exact effect sonication has on solids.

Cavitational effects involve the unsymmetrical collapse of cavitation bubbles near a solid surface producing localised microjets of high velocity liquids, high speed photography has provided evidence for this phenomenon. When aimed at a solid surface the microjets are able to produce severe surface damage, generate local heating and remove oxide coatings, which inhibit reaction at the metal surface. Shock waves formed as a result of cavitational collapse will cause the fractioning of solids. The resultant shock wave can increase the number of interparticle collisions which also aid particle fragmentation. Microstreaming will enhance liquid-surface mass transport and also cause solid particle collisions aiding size reduction.

Surface erosion due to microjet formation is also observed with large individual particles. The presence of surface defects induces cavitational collapse on the particle surface.

Suslick[50] has examined the sonochemical activation of several transition metals, iron, manganese, nickel and has obtained a dramatic enhancement in metal reactivity. Under sonicated conditions an active form of the metal salts is produced which will readily react with carbon monoxide, at low temperatures and pressures, to form carbonyl anions, precursors to many organic and organometallic compounds.

Nickel powder is usually inactive when hydrogenation of alkenes is attempted. Prior sonication of the nickel increases the hydrogenation capability of the powder by x10^5, with optimal hydrogenation achieved at 1 hour sonication[51]. The pre-sonicated powder appears to be more specific than Raney nickel as C-O bonds are not reduced on hydrogenation. One important factor to be noted is that the actual particle size of the nickel is not reduced when sonicated.

The irradiation of copper in terms of surface structure was examined[52]. It is thought that due to the spherical nature of the copper powder fragmentation and particle size reduction does not occur due to the higher structural strength. However the actual surface of the copper was altered. Copper powder initially has a thick oxide layer. After 1 hour sonication the surface becomes smooth but is still copper oxide, there was no pitting present suggesting that smoothing was not due to microjets. On further sonication the copper oxide layer cracks and is removed exposing 'cleaned' metal surface. Interparticle collisions due to microstreaming are thought to achieve this result.

Lindley et al[23] employed copper powder in the Ullmann Coupling reaction. Pre-sonication of the powder resulted in what was assumed to be a cleaning of the surface. Investigation of the particle size of the copper bronze during pre-sonication indicated a 53% size reduction within the first 15 minutes of sonication with upto 73% size reduction after 1 hour. Rate increases were associated with the increase in copper surface area obtained on particle size reduction. However size reduction alone could not explain the rate increases observed and an increase in mass transfer of products/ reactants at the surface of the metal powder during sonication was invoked to accommodate the results.

Mason et al[53] examined the particle size reduction of copper bronze in water and monitored the effects of changes in gas, temperature, volume and frequency. The largest particle size reductions were observed at low temperatures and with low frequency sonication (approximately 20kHz) in the presence of argon, a mono atomic gas with a high specific heat ratio.

Particle size reduction has been observed with large particle sizes of copper, see above, however with small diameter spherical powders fracture and particle size reduction is less likely. Suslick[54] continued his examination of sonication and its effect on solid morphology and surface composition by investigating the effect sonication has on copper and nickel metal powders. Nickel powder of two diameters, 5μm and 160μm, was irradiated. A smoothing of the solid surface was observed and significant agglomeration of the smaller particles occurred. The highly crystalline surface of nickel becomes smoothed after 1 hour of sonication as the depth of the metal oxide layer becomes reduced. By observing the surface morphology of the metal it was observed that the oxide layer appears to be 'chipped off' due to interparticle collisions. On continued sonication aggregation of the individual particles occurs as enough energy is present on collision of nickel particles to enable fusion to occur at the point of contact. A similar trend was observed with copper powder indicating the occurrence of high speed interparticle collisions. The less crystalline copper powder has a partial oxide surface coating which was totally removed during sonication and replaced with carbon, as yet no explanation exists for this phenomenon.

Aggregate formation also occurs on the sonication of other metals such as chromium and molybdenum[55]. Scanning electron micrographs before and after sonication indicated extensive agglomeration occurring due to fusion of the metal particles in zinc, chromium and nickel powders with surface smoothing also present. Molybdenum produced some agglomeration but not a significant effect. Whereas tungsten with its higher melting point of 3410°C exhibited no agglomeration at all. From all respective melting points it can be deduced that the temperatures required for efficient metal fusion must be between 2600°C and 3400°C.

Transition metals being quite malleable show smoothing of the surface and do not fragment, rate enhancement is probably due to exposure of 'fresh' metal surface.

Powdered inorganic solids being quite brittle should fragment easily, with rate enhancement being due to a considerable increase in surface area.

Suslick[21] examined the effect of sonication on brittle inorganic solids such as TaS_2 and MoO_3. Due to the brittle friable nature of the materials a large degree of surface pitting and erosion was observed. A significant decrease in particle size occurred, initial sizes approximately 60 - 90μm diameter were reduced to between 5 - 10μm, after which no further size reduction was observed even on prolonged irradiation.

Aoki et al[56] investigated the ultrasonic dispersion of several SiC powders. Initial powders of average diameter 30 - 100nm were agglomerated to particles of sizes approximately 300 - 500nm in diameter. In the presence of cavitation the agglomerates were effectively dispersed. The disruption of these agglomerates increased with power increase and also with an increase in the concentration of the powder. It is thought that the concentration effect is due to the increase in the probability of particle collisions due to shock waves and microstreaming to result in a more effective fragmentation of the solids. On prolonged irradiation reagglomeration appears to occur.

Particle size reduction was shown to occur in powdered inorganic solids[21]. Particles of 60-90μm diameter were reduced to 5-19μm after a few minutes of sonication, increasing the surface area considerably. Excess irradiation did not reduce the particle size further. This was thought to be due to the fact that microjets can only form at surfaces between 10-100 microns in diameter and shock waves do not affect smaller particles as much.

Chatakondu et al[57] investigated intercalcation reactions, the incorporation of organic or inorganic molecules into a layered inorganic host, with a view to observing a rate enhancement in the presence of ultrasound. In the presence of sonication the host solid initially decreases in size from 60-90μm to approximately 5μm after 15 minutes and although further size reduction is not achieved the surface continues to 'disintegrate' with surface area increasing continuously up to 45 minutes of sonication. However the reaction rate depends more on particle size reduction than on the subsequent surface damage.

Finally Thibert et al[58] compared the particle size reduction achieved via sonication to that by jet mill. Size reduction of salbumol crystals by sonication produced crystals 10 times smaller, with an average size 6μm. The sonified crystals had better flow properties and resembled the original crystals with corners and edges still present. Crystals obtained by jet mill are more rounded with an average size of 1μm but they tended to cluster and stick to solid surfaces. Sonication produces particles with different properties to those obtained by more mechanical means.

The above results confirm that heterogeneous reactions are much more complex when subjected to sonication and rate increases need not be due to simple solid size reduction.

4.2 EXPERIMENTAL CONDITIONS

4.2.1 Optimisation of sonochemical reaction conditions

The 'standard' O-alkylation reaction about which all further reactions were to be based is as described in section 2.2.1

Solvent Alterations

The standard reaction conditions as stated in section 2.2.1 were employed for thermal and sonicated reactions however the solvent present was altered from NMP (N-methylpyrrolidinone) to decalin (decahydronaphthalene), MEK (butan-2-one) and MIBK (2-methylpropan-2-one).

Volume Alterations

The standard reaction conditions, see section 2.2.1, were employed and the reagent concentration within the solvent was kept constant. However the reaction volume was altered to 75cm^3, 100cm^3, 125cm^3 or 150cm^3.

Concentration Alterations

In this series of reactions the reaction volume was kept constant as was the reagent stoichiometry. The standard reaction conditions, see section 2.2.1, quoted 5g (0.041 mols) of 2,6-dimethylphenol and this series of reactions will be based upon this. Multiples of this value will be employed. The concentration within 100cm^3 of solvent was varied as follows:-

x1.50 - contained 7.5g of 2,6-dimethylphenol

x1.00 - contained 5.0g of 2,6-dimethylphenol

x0.75 - contained 3.75g of 2,6-dimethylphenol

x0.50 - contained 2.50g of 2,6-dimethylphenol

and finally x0.25 - contained 1.25g of 2,6-dimethylphenol

Power Input Alterations

The sonicated reaction was repeated as for section 2.2.1 however the power introduced to the system via the John Perkins Sonic Systems 1.2cm diameter tip probe was varied as follows:-

5% output at setting 4.25

10% output at setting 6.00

15% output at setting 7.75 - the base reaction conditions

20% output at setting 8.75

25% output at setting 9.75.

4.2.2 Experimental conditions for base alterations

2,6-dimethylphenol

The standard reaction conditions were employed, see section 2.2.1, however the reaction was repeated substituting potassium carbonate with a series of bases at 50°C. Hydrated potassium carbonate, sodium carbonated, sodium hydrogen carbonate and lithium carbonate were used.

The reaction was also repeated thermally at 50°C with 2,6-dihydroxyacetophenone and 2,4-dihydroxyacetophenone altering the bases as above.

4.2.3 Experimental conditions for the O-alkylation of 2,6-dihydroxyacetophenone

The standard experiment was performed as for section 2.2.1.

4.2.4 Experimental conditions for the O-alkylation of 2,4-dihydroxyacetophenone

The standard experiment was performed as for section 2.2.1.

4.2.5 Experimental conditions for halide alterations

2,6-dimethylphenol

The standard experiment was performed as for section 2.2.1 at 50°C and the reaction was repeated with 10.08g (0.082 mols) of 1-bromopropane.

2,6-dihydroxyacetophenone

The standard experiment was performed as for section 2.2.1 and the reaction was repeated with 6.46g (0.052 mols) of 1-bromopropane. The thermal reaction employed the same reagents.

2,4-dihydroxyacetophenone

The standard experiment was performed as for section 2.2.1 and the reaction was repeated with 6.46g (0.052 mols) of 1-bromopropane. The thermal reaction employed the same reagents.

4.2.6 Experimental conditions for temperature alterations - thermal reactions

The standard 2,6-dihydroxyacetophenone thermal reaction, see section 2.2.1, was performed at 65°C. The experiment was also repeated at 50°C.

The above experiment was also repeated with 2,4-dihydroxyacetophenone.

4.2.7 Reaction with micronised potassium carbonate

The sonicated reaction conditions were employed as for section 2.2.1 but micronised potassium carbonate was employed as the base.

4.2.8 Extended reaction conditions

The standard reaction conditions were employed, see section 2.2.1, but the sample was irradiated for an extended period of 6 hours.

The thermal reaction employed the same reaction conditions as above. Samples were withdrawn hourly and the reaction was run overnight to 24 hours reaction time in an effort to bring it to completion. Sample preparation and analysis was as above.

4.2.9 Reaction with 1,3-dibromopropane

The reaction conditions employed were as for section 2.2.2 but the alkyl halide was altered to 2.62g (0.013 mols) of 1,3-dibromopropane. In this case all analysis was performed by HPLC. The thermal reaction employed the same reagents as above.

4.2.10 Reaction with Epichlorohydrin

The reaction conditions employed were as for section 2.2.3.

4.3 ANALYSIS CONDITIONS

4.3.1 GLC CONDITIONS

4.3.1.1 GLC Conditions for 2,6-dimethylphenol

The Shimadzu GC Mini 2 chromatograph with integrator was employed with an SE30 stainless steel column (length 2m, diameter 0.5cm).

Initial Column Temperature	130°C
Injector/ Detector Temperature	180°C
Injected Volume	2μl
Running Time	10 mins
Nitrogen Pressure	14

Retention times

Ethyl acetate	0.9 mins
1-iodopropane	1.16 mins
N-methylpyrrolidinone	3.31 mins
2,6-dimethylphenol	4.38 mins
2,6-dimethyl-1-propoxybenzene	7.58 mins

4.3.1.2 GLC Conditions for 2,6-dihydroxyacetophenone and 2,4 dihydroxyacetophenone

The Shimadzu GC Mini 2 *chromatograph with integrator was employed with* an OV17 stainless steel column (length 2m, diameter 0.5cm).

Initial Column Temperature	200°C
Injector/ Detector Temperature	250°C
Injected Volume	2μl
Running Time	10 mins
Nitrogen Pressure	14

Retention times

Ethyl acetate	0.62 mins
N-methylpyrrolidinone	0.92 mins
2,6-dihydroxyacetophenone	2.57 mins
2-hydroxy-6-propoxyacetophenone	4.03 mins
2,4-dihydroxyacetophenone	3.34 mins
2-hydroxy-4-propoxyacetophenone	7.83 mins

4.3.2 HPLC CONDITIONS

The equipment employed was the Hewlett Packard 1090L (series 1) Hewlett Packard filter photometric detector with Hewlett Packard 3396 integrator using the INET command system.

HPLC Solvent Composition

Mobile Phase Solvent A -

50cm^3 of stock acetate buffer diluted to 1000cm^3 with HPLC grade water.

Mobile Phase Solvent B -

50 cm^3 of stock acetate buffer diluted to 700cm^3 with HPLC grade acetonitrile and then diluted further to 1000cm^3 with HPLC grade water.

Stock Acetate Buffer -

136.1g HPLC grade sodium acetate trihydrate in 800cm^3 HPLC grade water. Adjust to pH4.5 with HPLC grade acetic acid and then dilute to 1000cm^3 with further HPLC grade water.

4.3.2.1 O-alkylation of 2,6-dihydroxyacetophenone with 1,3-dibromopropane

15cm ODS General Use HPLC Column

Solvent Flow	1.5cm/min
Max Pressure	400 bar
Min Pressure	50 bar
Oven Temperature	45°C
Injected Volume	5μl
Attenuation	6
Detector wavelength	254nm

Solvent composition during analysis run

When time = 0 mins % solvent B = 25

time = 3 mins %B = 25

time = 15 mins %B = 70

time = 25 mins %B = 95

time = 30 mins %B = 95

time = 35 mins %B = 70

time = 37 mins %B = 25

Retention times

2,6-dihydroxyacetophenone	4.81 mins
2-hydroxy-6-propoxybromideacetophenone	16.35 mins
Dihydroxyacetophenone diether of 1,3-dibromopropane	19.09 mins

4.3.2.2 O-alkylation of 2,6-dihydroxyacetophenone with epichlorohydrin

15cm ODS General Use HPLC Column

Solvent Flow	1.5cm/min
Max Pressure	400 bar
Min Pressure	50 bar
Oven Temperature	45^{o}C
Injected Volume	5μl
Attenuation	6
Detector wavelength	254nm

Solvent composition during analysis run

When time = 0 mins % solvent B = 25

time = 3 mins %B = 25

time = 15 mins %B = 70

time = 25 mins %B = 70

time = 27 mins %B = 25

Retention times for reaction in 4-methylpentan-2-one

2,6-dihydroxyacetophenone	4.55 mins
Intermediate 1	8.57 mins
Intermediate 2	9.15 mins
Final Product	14.05 mins

Retention times for reaction in dimethylformamide and N-methypyrollidinone

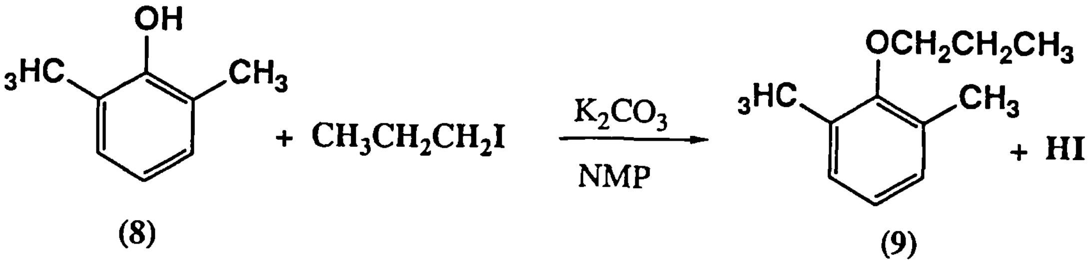
2,6-dihydroxyacetophenone	5.90 mins
Intermediate 1*	7.80 mins*
Intermediate 2	9.30 mins
Final Product	14.90 mins

* - A different intermediate to that present in 4-methylpentan-2-one.

4.4 RESULTS/ DISCUSSION

4.4.1 REACTIONS OF 2,6-DIMETHYLPHENOL

To study exclusively the O-alkylation of phenols means that C-alkylation must be negligible. The standard reaction studied for the O-alkylation of phenols was taken to be the O-alkylation of 2,6-dimethylphenol (8) with 1-iodopropane in the presence of potassium carbonate base to give the aryl ether (9).



C-alkylation is reduced by blocking the ortho carbons at which alkylation is likely to occur.

Optimisation of the thermal O-alkylation reaction was undertaken in a final year undergraduate project by A.Moore[59] with best yields obtained at the reaction temperature of 65°C and with an initial reagent ratio of phenol: alkyl halide: base as 1:2:2. The optimisation of thermal reaction conditions involves the consideration of temperature, stirring rate, reagent solubility and base particle size.

In the case of optimisation of a sonicated reaction this also involves the consideration of factors such as power input, reaction volume and even reaction concentration as all these factors effect the efficiency of ultrasound within the reaction medium. The optimisation of the O-alkylation of 2,6-dimethylphenol was studied with a view to considering the above factors.

4.4.1.1 Solvent Alterations

It was thought that solvents with low vapour pressures and high boiling points would result in much more effective cavitational collapse due to less solvent vapour diffusion into the cavitational void and hence reduced 'cushioning' of the cavitation bubble. The solvents chosen for study were N-methylpyrrolidinone (b.p. 202°C), butan-2-one (b.p. 79.6°C), 4-methylpentan-2-one (b.p.117°C) and decahydronaphthalene (decalin) (b.p. 190°C) see Table. 4.1 and Fig. 4.1.

Table. 4.1 - % Conversion of 2,6-dimethylphenol with respect to solvent type and sonication time at 15% output power at 65°C.

	SOLVENT			
TIME	NMP	MEK	MIBK	DECALIN
30 mins	34.5%	2.48%	0.77%	-
60 mins	36.0%	2.82%	0.84%	-
90 mins	59.6%	3.50%	0.89%	-

NMP - N-methylpyrrolidinone
MEK - Butan-2-one (Methyl ethyl ketone)
MIBK - 4-Methylpentan-2-one (Methyl isobutyl ketone)

From the boiling points of the solvents the most effective rate enhancement should be in N-methylpyrrolidinone as this solvent would have the lowest vapour pressure and should support cavitation most effectively. Assuming that argument is correct butan-2-one with the highest vapour pressure should result in the least rate enhancement, with the other solvents in between. As the reaction studied was a heterogeneous reaction it could be assumed that some of the increase in reaction rate may be due to a decrease in base particle size with an increase in base surface area. The study of heterogeneous reactions in the presence of sonication and the effect sonication has on particle size has been well documented (see earlier).

Particle size reduction could be a good measure of the efficiency of cavitation within the solvent. Results obtained from another undergraduate project[60] indicated that N-methylpyrrolidinone (NMP) and decalin supported similar rates of base particle size reduction while butan-2-one and 4-methylpentan-2-one did not support any particle size reduction at all, as would be expected when considering vapour pressure.

However it would seem that vapour pressure was not the only factor to come into play when considering the rate of % conversion of the phenol to the O-alkylated product ether. It can be seen that the most effective rate was indeed observed in N-methylpyrrolidinone however unexpectedly decalin, which exhibited particle size reduction of base and has a low vapour pressure, showed no conversion whatsoever thermally or when under sonication.

4.4.1.2 Temperature Alterations

For a thermal first order reaction a 10°C increase in temperature results in a doubling of reaction rate. However this does not hold true for sonicated reactions according to Noltingk and Neppiras[3] a decrease in temperature results in a more effective cavitation bubble collapse. This is due to less solvent vapour diffusion into the cavity, a direct reference to the solvent vapour pressure being low at lower temperatures. Thus when the sonicated reaction was compared to the thermal reaction (see Table. 4.2) the greatest rate enhancement was seen between the lower temperatures of reaction (see Fig. 4.2). At higher temperatures cavitation effects will diminish, due to the reasons explained above, rate enhancement over thermal conditions will be reduced.

Fig 4.1 - Effect of solvent alterations on % Conversion of 2,6-dimethylphenol

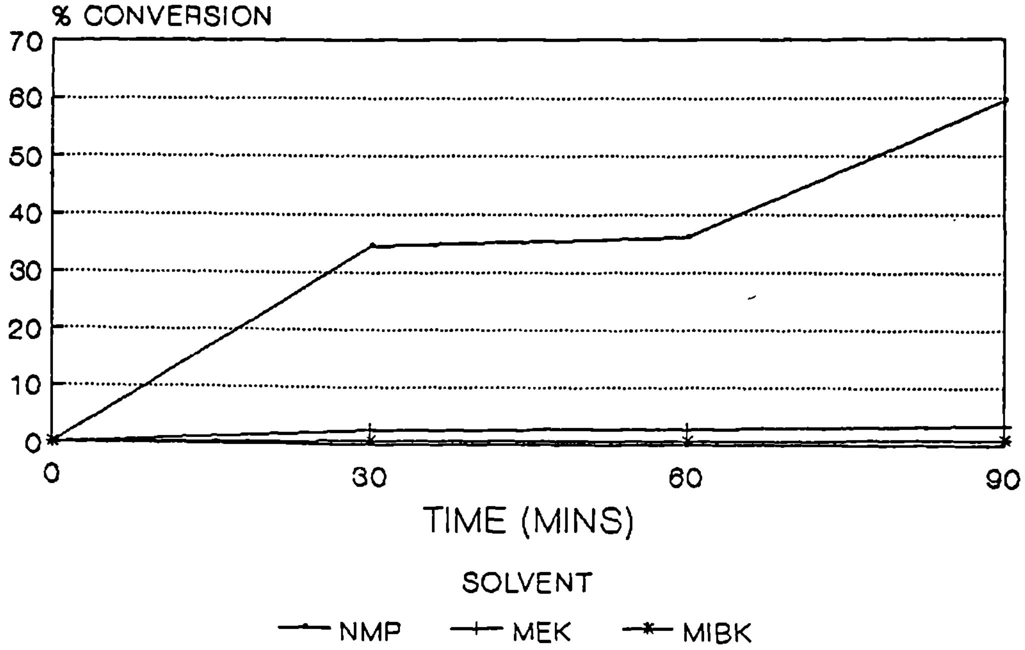


Fig 4.2 - Effect of temperature alterations on % Conversion of 2,6-dimethylphenol

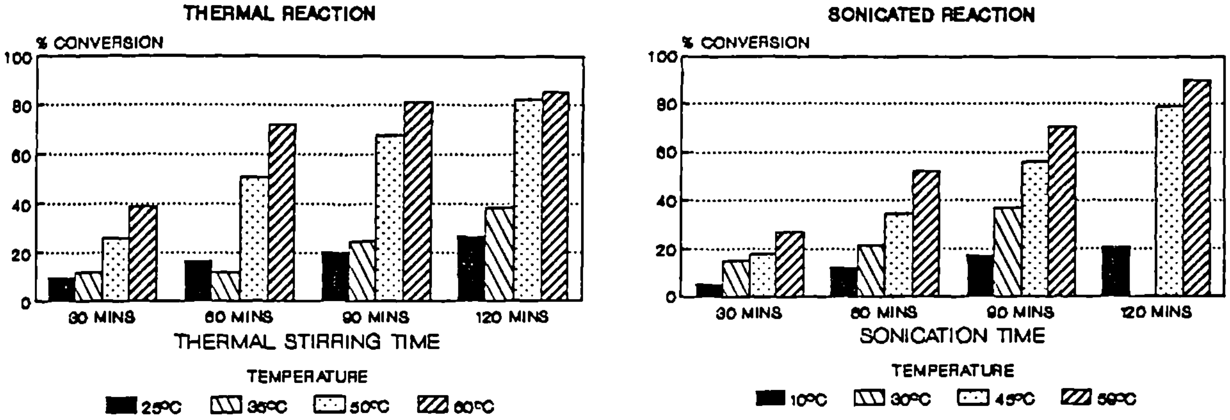


Table. 4.2 - % Conversion of 2,6-dimethylphenol with respect to temperature and sonication time.

	TEMPERATURE							
	THERMAL				**SONICATED**			
TIME	**25°C**	**35°C**	**50°C**	**60°C**	**10°C**	**30°C**	**45°C**	**59°C**
30 mins	9.9%	12.1%	26.0%	38.9%	5.6%	14.9%	17.7%	27.4%
60 mins	16.9%	12.1%	51.0%	72.0%	12.3%	21.7%	35.0%	52.2%
90 mins	20.7%	24.9%	67.8%	81.5%	17.5%	37.0%	55.9%	70.5%
120 mins	27.5%	38.6%	82.6%	85.5%	21.3%	-	78.8%	90.1%

4.4.1.3 Volume Alterations

If the amount of power entering the system is taken to be constant, then as the volume of the reaction is increased, the intensity of ultrasound per cm^3 will decrease and the rate of reaction should fall and vice versa (see Table. 4.3 and Fig. 4.3).

Table. 4.3 - % Conversion of 2,6-dimethylphenol with respect to reaction volume and sonication time.

	VOLUME			
TIME	**75cm^3**	**100cm^3**	**125cm^3**	**150cm^3**
30 mins	21.9%	16.3%	9.6%	4.2%
60 mins	39.8%	31.4%	19.1%	9.1%
90 mins	67.8%	60.6%	43.5%	31.5%

There will come a point where sonication will have little or no effect on the reaction, as the solvent volume becomes too great. The reverse may also occur when sonication can have too much effect. Studies at 50cm^3 and 25cm^3 of solvent were not undertaken due

Fig 4.3 - **% Conversion of 2,6-dimethylphenol with respect to reaction volume and sonication time**

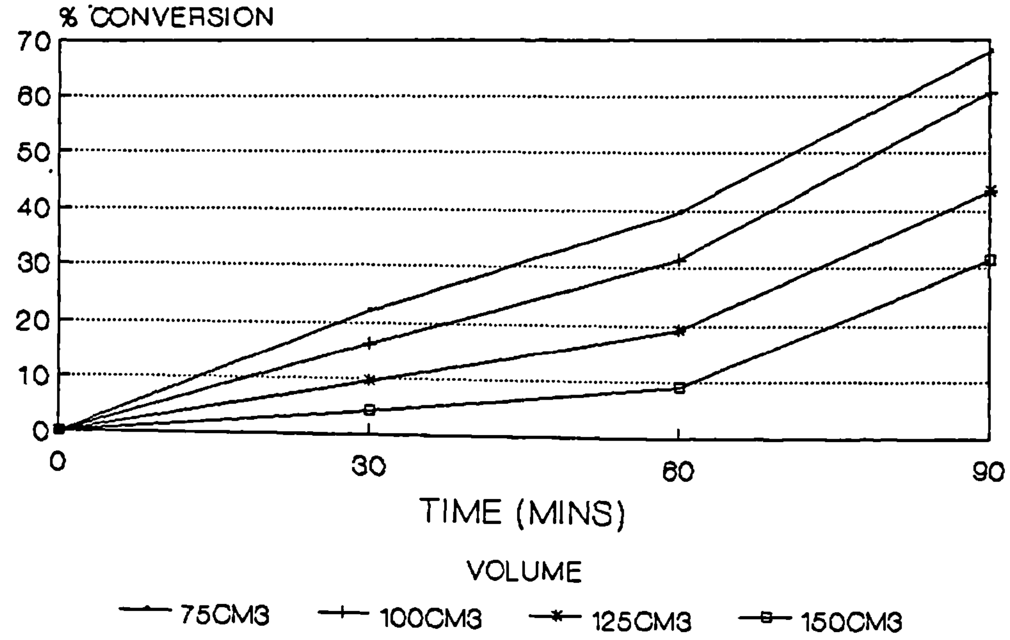
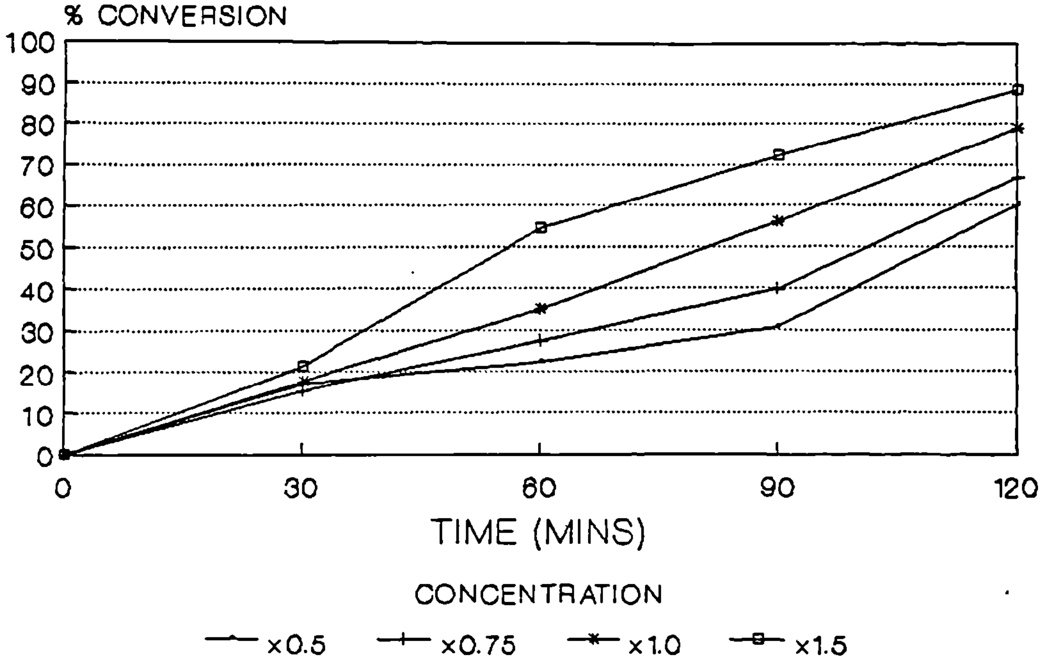


Fig 4.4 - **% Conversion of 2,6-dimethylphenol with respect to reaction concentration and sonication time**



to the fact that not enough solvent was present to support cavitation effectively. Too much power entering a small volume would have the effect of 'tearing' the solvent apart during the rarefaction cycle and vapourising it, especially with solvents of high vapour pressure. As the reaction volume was decreased an increase in reaction rate was observed.

4.4.1.4 Concentration Alterations

If it is assumed that reaction rate enhancement is due to the effects of cavitation, it must also be assumed that cavitation will have a stronger result in more concentrated solutions simply due to the fact that the likelihood of a cavitational collapse involving a substrate will be increased (see Table. 4.4 and Fig. 4.4).

Table. 4.4 - % Conversion of 2,6-dimethylphenol with respect to reagent concentration and sonication time.

	CONCENTRATION			
TIME	**x0.5**	**x0.75**	**x1.0**	**x1.5***
30 mins	17.1%	15.5%	17.7%	21.4%
60 mins	22.4%	27.4%	35.0%	54.3%
90 mins	30.4%	39.7%	55.9%	72.2%
120 mins	60.1%	66.8%	78.8%	88.4%

* - Concentrations have been explained.

The more effective the diffusion of the reactants into the cavitation bubble in preference to solvent vapour, the greater the rate increase due to the high temperatures and pressures reached. If rate enhancement is due to an increase in potassium carbonate surface area, then increasing the probability of cavitation implosion on or near the base will increase the reaction rate. This probability is increased with an increase in reagent concentration within the reaction medium. An increase in reaction concentration resulted in an increase in reaction rate.

4.4.1.5 Power Alterations

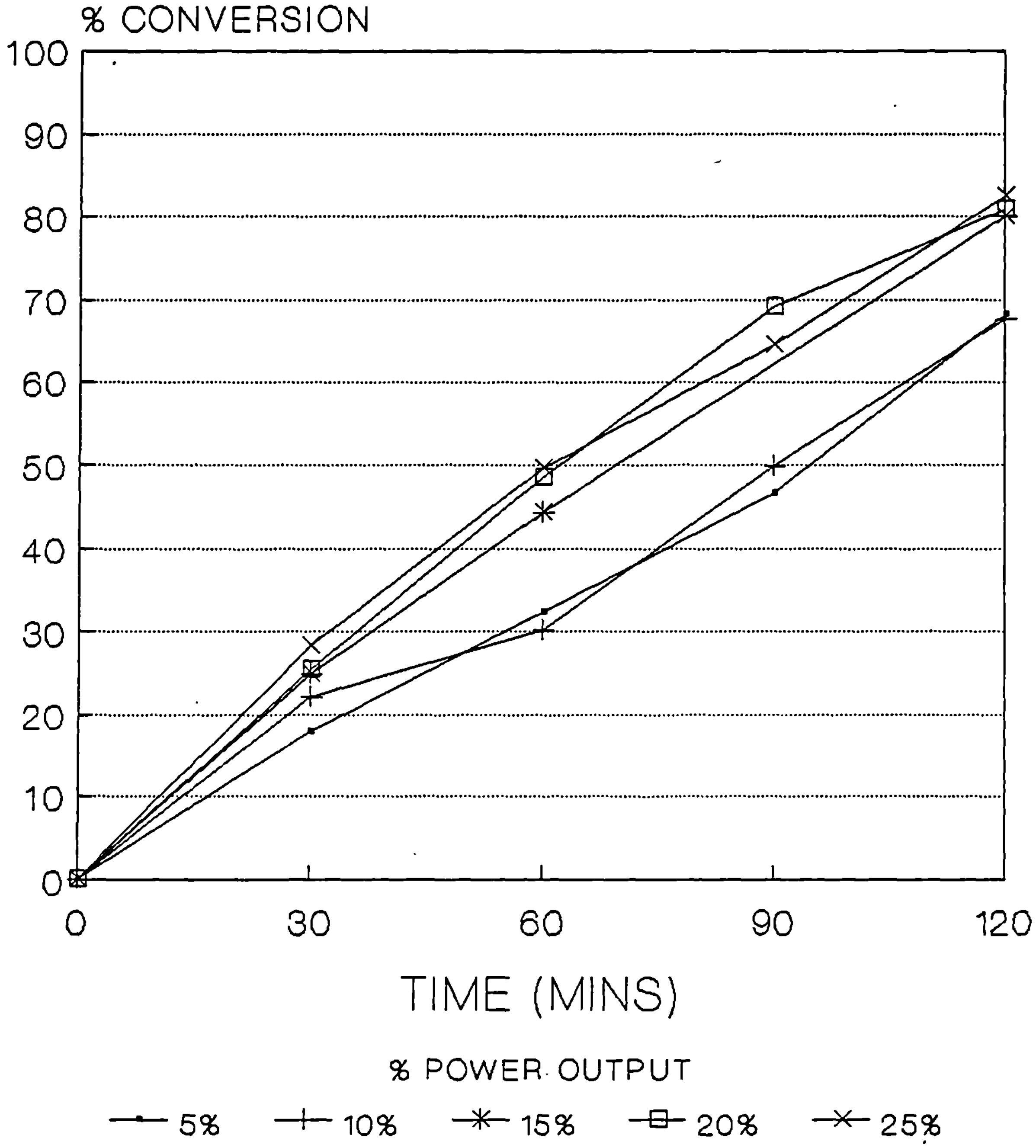
It was stated earlier that an increase in reaction rate depended upon the solvent's ability to support cavitation. Rate enhancement due to cavitation can only occur if cavitation is indeed present. Each solvent will have a cavitation threshold below which cavitation bubbles are not formed, although efficient mixing and mass transfer may be present. The amount of power entering the system is important as the cavitation threshold may or may not be reached. It was thought that the examination of the O-alkylation of 2,6-dimethylphenol with a view to altering the amount of power entering the system would give an indication to the cavitation threshold within N-methylpyrrolidinone (Table. 4.5 and Fig. 4.5).

Table. 4.5 - % Conversion of 2,6-dimethylphenol with respect to sonication time and sonication % power output.

	% POWER OUTPUT				
TIME	**5%**	**10%**	**15%**	**20%**	**25%**
30 mins	17.9%	22.1%	24.8%	25.4%	28.3%
60 mins	32.3%	30.2%	44.4%	48.6%	49.6%
90 mins	46.6%	49.9%	51.1%	69.1%	64.5%
120 mins	68.2%	67.7%	80.0%	80.9%	82.5%

When the power introduced into the system is sufficient to pass the threshold, and efficient cavitation bubbles are present, a sharp increase in rate should be observed. This

Fig 4.5 - % Conversion of 2,6-dimethylphenol with respect to power applied and sonication time



was seen when 15% power output at a 7.75 setting was employed. Another observation was also made. Once the cavitation threshold was passed further increases in rate were not observed. This can be explained in terms of 'overcavitation'. A comparison to cavitation within small amounts of solvent volumes could be made. Increasing the amount of power entering the solvent medium resulted in increasing the amount of cavitation bubbles formed. A threshold was reached where the amount of solvent present could not support the amount of cavitation required of it. Thus the maximum rate enhancement due to cavitation was reached and further increases in power input would be wasted. This could be seen in Fig. 4.5.

4.4.1.6 Base Alterations

In aprotic solvents with low dielectric constants the base cation is probably part of an associated pair with the phenoxide ion[48]. With a small cation such as lithium these ion pairs will be 'tight' and O-alkylation minimised. The ion pairs will become 'looser' as you pass from lithium to sodium to potassium. The cation's positive charge is spread over a larger volume resulting in the electrostatic resistance to O-alkylation being reduced. In low dielectric aprotic solvents the influence of the cation is large.

Aprotic high dielectric solvents are very effective in solvating the cation however not as effective in solvating the anion. Lithium ions with a high concentration of positive charge will be more efficiently solvated and the positive charge dispersed throughout the surrounding medium. Potassium will be least solvated due to its already weaker concentration of positive charge. Some phenoxide anions probably exist as 'free' anions due to the ineffective solvation of the solvent and are very reactive. With the oxygen anion dissociated from a corresponding cation O-alkylation will be very effective. Thus in high dielectric solvents the nature of the cation is not as important.

N-methylpyrrolidinone is an aprotic solvent with a high dielectric constant 32.0, compared to tetrahydrofuran which has a low dielectric constant of 7.58. It was therefore expected that the cation of the base catalyst employed within the reaction would not play a large part in altering the reaction rate. Results obtained from examination of a series of base types with respect to their O-alkylation abilities (see Table. 4.6) indicated, completely unexpectedly, that a change in cation results in a change in reaction rate.

Table. 4.6 - % Conversion of 2,6-dimethylphenol under thermal conditions at 50°C with respect to base type and reaction time.

	BASE TYPE				
TIME	**K_2CO_3**	**$K_2CO_3.H_2O$**	**Li_2CO_3**	**$NaHCO_3$**	**Na_2CO_3**
30 mins	22.4%	17.7%	0%	1.88%	1.9%
60 mins	32.4%	34.6%	0%	4.23%	4.3%
90 mins	40.7%	31.0%	0%	4.35%	5.1%
120 mins	51.3%	44.7%	0%	4.67%	7.8%

Fastest rates of reaction occurred with a potassium cation and slowest with lithium cation, this would be a perfect example for a low dielectric reaction. Thus it can be stated that in the O-alkylation system studied the presence of N-methylpyrrolidinone solvent indicated that other factors must influence the reaction, not only the dielectric ability and aprotic nature of the solvent. These results were confirmed when the O-alkylations of 2,4-dihydroxyacetophenone and 2,6-dihydroxyacetophenone were attempted in N-methylpyrrolidinone with a series of bases (see Tables. 4.7 -> 4.9).

Table. 4.7 - % Conversion of 2,6-dimethylphenol under sonicated conditions at 50°C with respect to base type and reaction time.

	BASE TYPE				
TIME	K_2CO_3	$K_2CO_3.H_2O$	Li_2CO_3	$NaHCO_3$	Na_2CO_3
30 mins	71.1%	20.4%	0.46%	1.34%	8.6%
60 mins	59.1%	23.0%	0.55%	5.23%	11.1%
90 mins	72.2%	27.5%	0.85%	5.49%	14.85%

Table. 4.8 - % Conversion of 2,6-dihydroxyacetophenone under thermal conditions at 50°C with respect to base type and reaction time.

	BASE TYPE				
TIME	K_2CO_3	$K_2CO_3.H_2O$	Li_2CO_3	$NaHCO_3$	Na_2CO_3
60 mins	6.4%	4.8%	-	-	-
120 mins	19.1%	22.4%	-	-	2.9%
180 mins	43.4%	44.3%	-	-	7.7%

Table. 4.9 - % Conversion of 2,4-dihydroxyacetophenone under thermal conditions at 50°C with respect to base type and reaction time.

	BASE TYPE				
TIME	K_2CO_3	$K_2CO_3.H_2O$	Li_2CO_3	$NaHCO_3$	Na_2CO_3
30 mins	42.1%	6.4%	0.32%	0.16%	2.18%
60 mins	59.7%	21.0%	0.20%	0.24%	4.60%
90 mins	58.9%	33.9%	0.31%	0.53%	4.80%

The O-alkylation of 2,6-dihydroxyacetophenone and 2,4-dihydroxyacetophenone was only studied by the rate of disappearance of the starting material.

2,6-dihydroxyacetophenone may undergo alkylation at either the 2 or the 6-hydroxyl group, however as they are sterically and electronically identical the rates of attack at either position would be similar. Different rules exist for the 2,4-dihydroxyacetophenone. The 2-hydroxyl group will undergo steric and electronic hindrance caused by the adjacent carbonyl group. The 4-hydroxyl group will have reduced effects due to its distance away from the carbonyl. The rate of alkylation at the 4-hydroxyl group should be faster than the rate of alkylation at the 2-hydroxyl group and the primary O-alkylation product would be expected to be the 2-hydroxy,4-propoxyacetophenone. This however was not positively confirmed. Dialkylation at both hydroxyls was also thought to occur however this was also not confirmed.

4.4.1.7 Halide Alterations

The influence of the leaving group on alkylation reactions can be examined by changing the halide ion from iodide to bromide. The iodine ion, due to its more dispersed negative charge would be a better leaving group, as it is not as closely held to the corresponding alkyl cation. This suggests that a faster rate of alkylation should occur with 1-iodopropane than with 1-bromopropane, if no other factors come into play.

Results obtained on alkylation of 2,6-dimethylphenol, 2,4-dihydroxyacetophenone and 2,6-dihydroxyacetophenone with 1-iodopropane and 1-bromopropane proved to be completely inconclusive (see Tables Nos 4.10 -> 4.12). 2,6-dimethylphenol and 2,6-dihydroxyacetophenone had a faster rate of conversion with 1-bromopropane with only 2,4-dihydroxyacetophenone giving the expected rate increase with 1-iodopropane.

Table. 4.10 - % Conversion of 2,6-dimethylphenol under sonicated conditions at approximately 55°C with respect to base, alkyl halide and reaction time.

	BASE TYPE			
	K_2CO_3		$K_2CO_3.1.5H_2O$	
TIME	**1-Iodo**	**1-Bromo**	**1-Iodo**	**1-Bromo**
30 mins	17.7%	9.9%	22.4%	11.1%
60 mins	34.6%	22.8%	32.4%	17.7%
90 mins	31.0%	36.1%	40.7%	27.5%
120 mins	46.5%	65.6%	69.5%	69.5%

Table. 4.11 - % Conversion of 2,6-dihydroxyacetophenone with respect to time and mode of reaction at 65°C and the effect of halide change.

	1-Iodopropane		**1-Bromopropane**	
TIME	**Thermal**	**Sonicated**	**Thermal**	**Sonicated**
30 mins	-	12.5%	-	42.8%
60 mins	6.4%	29.9%	-	63.2%
90 mins	-	44.0%	-	68.2%
120 mins	19.1%	-	26.2%	71.4%
180 mins	43.5%	-	56.8%	77.1%
240 mins	-	-	64.4%	-

Table. 4.12 - % Conversion of a sonicated 2,4-dihydroxyacetophenone reaction at 65°C with respect to halide change.

	ALKYL HALIDE	
TIME	**1-Iodopropane**	**1-Bromopropane**
0 mins	-	-
30 mins	26.8%	6.4%
60 mins	51.1%	18.1%
90 mins	63.0%	29.7%

4.4.1.8 Effect of Temperature on a Thermal Reaction

It is known that an increase in the temperature of a thermal reaction results in an increased reaction rate. The rate of thermal O-alkylation at 50°C and 65°C was examined (see Tables Nos 4.13 - 4.14).

Table. 4.13 - % Conversion of thermal 2,6-dihydroxyacetophenone reaction with respect to temperature and reaction time.

	TEMPERATURE	
TIME	50°C	65°C
60 mins	9.1%	6.4%
120 mins	24.2%	19.1%
180 mins	32.7%	43.4%

Table. 4.14 - % Conversion of thermal 2,4-dihydroxyacetophenone reaction with respect to temperature and reaction time.

	TEMPERATURE	
TIME	50°C	65°C
60 mins	8.3%	42.1%
120 mins	25.8%	59.7%
180 mins	28.8%	58.9%

These reactions also indicated that an increase in temperature results in an increased rate. This may give an advantage over the corresponding sonicated reaction as sonicated reactions produce a more effective cavitational collapse at lower temperatures and this is where the advantages lie.

4.4.2 REACTIONS OF 2,6-DIHYDROXYACETOPHENONE

Further studies on the O-alkylation of 2,6-dihydroxyacetophenone were undertaken as this substance was of interest to Fisons Pharmaceuticals. The hydroxyacetophenone backbone is often used as a precursor to asthma drugs with Fisons asthma drug Intal (19) (see later) being a prime example.

4.4.2.1 Reaction with Micronised Potassium Carbonate

It has always been thought that an increase in catalyst/ base surface area will result in an increase in rate of reaction. Ultrasound is thought to aid heterogeneous reactions primarily by this route. Pre-micronised potassium carbonate was mechanically ground to small particle sizes and had an increased surface area when compared to granular potassium carbonate. Use of micronised base resulted in an increase in rate approximately 31 fold for the sonicated reaction and 6 fold for the conventional thermal reaction within the initial 30 minutes (see Tables Nos 4.15 - 4.16).

Table. 4.15 - % Conversion of 2,6-dihydroxyacetophenone under thermal reaction conditions at 65°C.

TIME	Normal K_2CO_3	Micronised K_2CO_3
60 mins	6.4%	39.8%
120 mins	19.1%	44.6%
180 mins	43.4%	51.9%

Table. 4.16 - % Conversion of 2,6-dihydroxyacetophenone under sonicated reaction conditions at 65°C.

TIME	Normal K_2CO_3	Micronised K_2CO_3
30 mins	0.18%	5.74%
60 mins	1.18%	11.59%
90 mins	3.40%	17.90%

After 90 minutes this increase in rate fell to a 5 fold enhancement with sonication and micronised base with equal rates of reaction for both base sizes observed for the thermal reaction.

4.4.2.2 Extended Thermal and Ultrasonic Reactions

Extended thermal and ultrasonic reactions were attempted in an effort to bring the O-alkylation of 2,6-dimethylphenol to completion (see Table. 4.17).

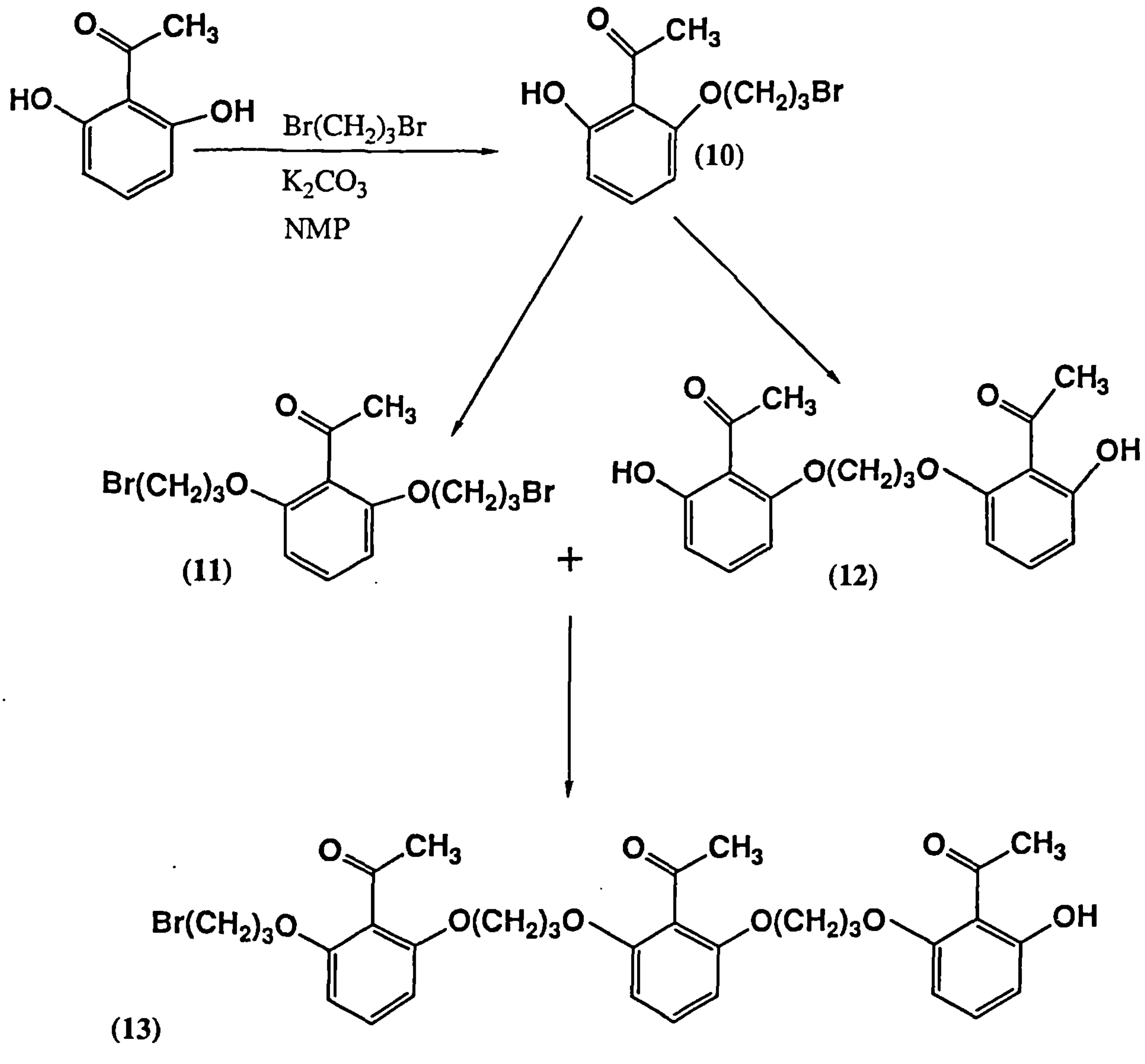
Table. 4.17 - % Conversion of 2,6-dihydroxyacetophenone with respect to mode of reaction and reaction time at 65°C.

TIME	THERMAL	SONICATED
0.5 hrs	-	41.6%
1.0 hrs	8.5%	57.0%
2.0 hrs	22.7%	-
3.0 hrs	32.6%	-
4.0 hrs	-	65.9%
5.0 hrs	46.7%	68.9%
6.0 hrs	49.1%	-
7.0 hrs	51.2%	-
Overnight	52.2%	-

It was noted that after 24 hours the thermal reaction mixture contained approximately 48% of starting material. The sonicated reaction, was initially faster than the thermal reaction (after 1 hour 48% starting material remained) but showed signs of slowing after this period with 34% remaining after 4 hours and only 31% after 5 hours sonication. It would seem that to bring this reaction to completion would require very long reaction times and probably several additions of 1-iodopropane and/ or base.

4.4.2.3 Alkylation with 1,3-dibromopropane

O-alkylation of 2,6-dihydroxyacetophenone with a dihaloalkane should provide a wider product distribution. Monoalkylation may occur with one alkyl attack on one hydroxyl group (10) and dialkylation may occur with two alkyl groups attacking both hydroxyl groups (11). Furthermore the alkyl halide itself may undergo electrophilic attack at either end resulting in two dihydroxyacetophenone groups being joined by a bridged alkyl group (12). Larger molecules may also form with three acetophenone groups joined (13).



As earlier, the initial reagent ratio was taken to be 1:2:2 of acetophenone: halide: base this however resulted in very complex HPLC and GLC spectra. The best results were obtained when the amount of 1,3-dibromopropane was reduced to a ratio of 2:1 of acetophenone: 1,3-dibromopropane (see Tables. 4.18 - 4.19). A steady decrease in starting material, 2,6-dihydroxyacetophenone, was observed which then began to level off. Samples taken at 24 hours and 5 days thermal reaction time still showed the presence of starting material.

Table. 4.18 - % Conversion of 2,6-dihydroxyacetophenone under thermal reaction conditions.

	% CONVERSION		
TIME	**Starting Material**	**Intermediate**	**Final Product**
1 - 3 mins	89.5%	9.0%	1.5%
15 mins	73.7%	16.6%	9.6%
30 mins	59.7%	17.6%	22.7%
60 mins	46.0%	14.3%	39.7%
90 mins	38.7%	10.6%	50.7%
180 mins	29.1%	3.8%	67.0%
240 mins	27.1%	2.7%	70.2%
300 mins	26.3%	1.5%	72.2%

Table. 4.19 - % Conversion of 2,6-dihydroxyacetophenone under sonicated reaction conditions.

	% CONVERSION		
TIME	**Starting Material**	**Intermediate**	**Final Product**
1 - 3 mins	98.7%	1.3%	-
15 mins	70.2%	21.3%	8.5%
30 mins	65.6%	25.7%	8.8%
60 mins	50.7%	24.9%	24.4%
90 mins	52.2%	21.6%	26.2%
180 mins	43.4%	10.4%	56.6%

The major product observed was isolated and identified as being the dihydroxyacetophenone diether of 1,3-dibromopropane (12). This product goes to 72.2% conversion after 5 hours thermal reaction time (see Fig. 4.6).

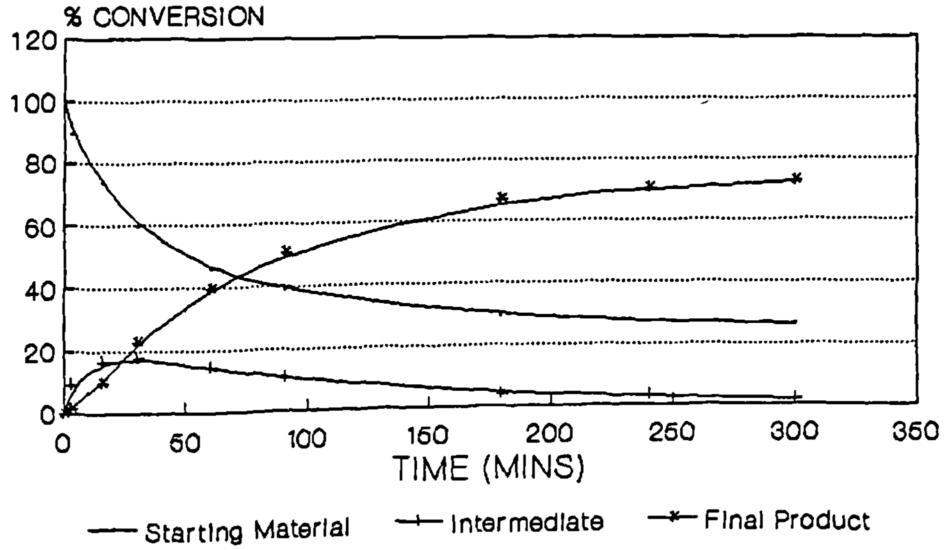
There was evidence to suggest the presence of an intermediate (see Fig. 4.6). A maximum conversion of 17.6% was reached by this substance after ½hour and this steadily decreased to approximately 1.5% at 5 hours reaction time. The intermediate was isolated and identified as being the mono-alkylated product of 2,6-dihydroxyacetophenone (10).

Two minor side products were observed one at 7.7% conversion, not identified even after mass spectral analysis, and the other at 2.1% conversion thought to be the larger ’trimer’ molecule.

Sonication produced a slower rate of conversion of the starting material 56.6% compared to 67% thermally after 3 hours, however a larger amount of intermediate was formed 25.7% compared to 17.6% after 30 minutes.

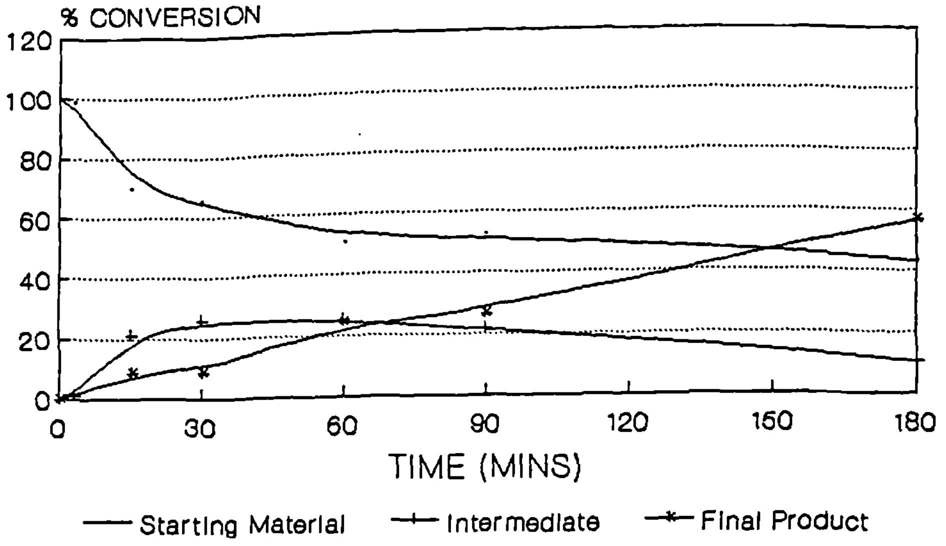
Fig 4.6 - Reaction of 2,6-dihydroxyacetophenone with 1,3-dibromopropane under thermal and sonicated conditions

Thermal Reaction



RATIO 1: 5: 5

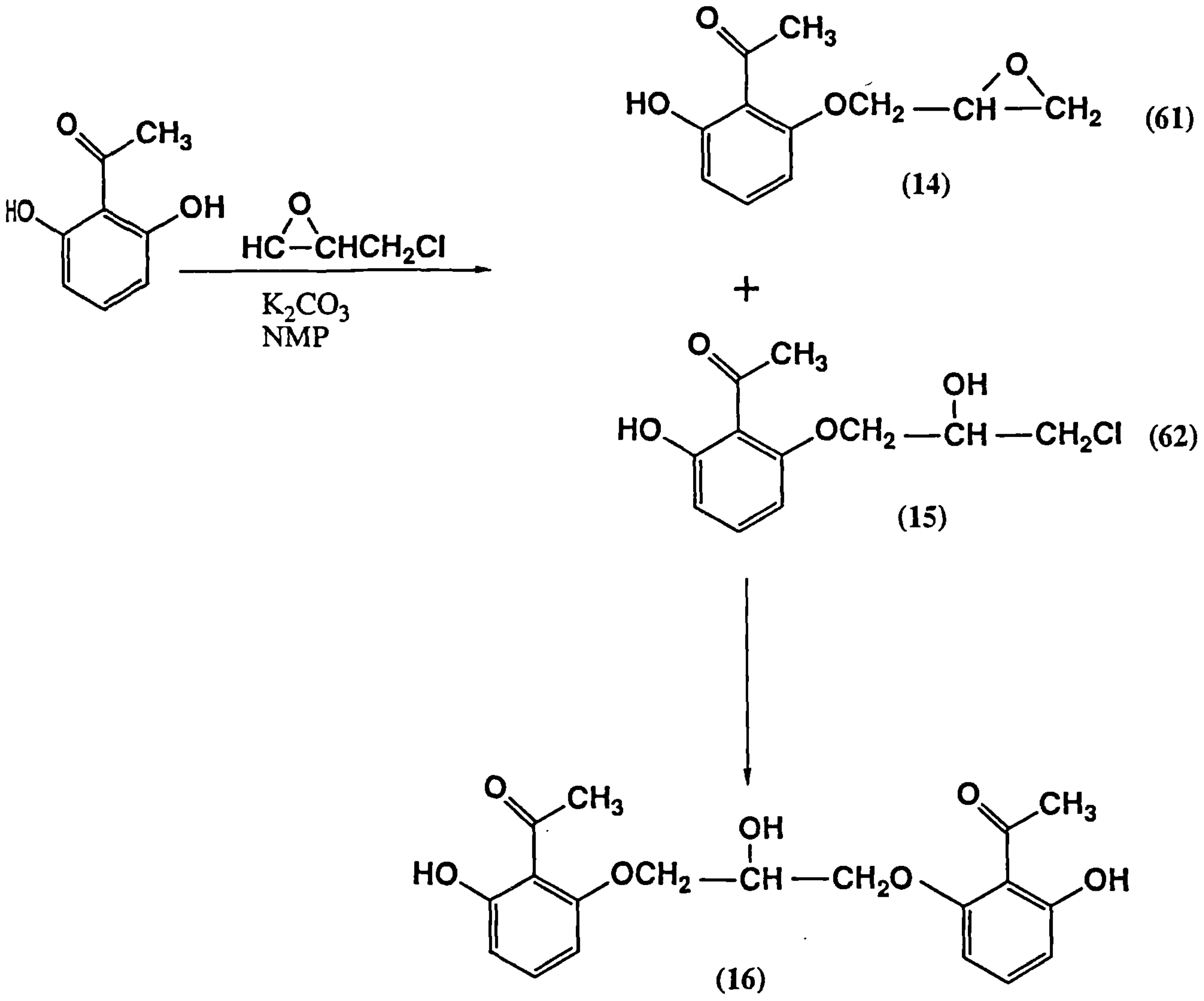
Sonicated Reaction



RATIO 1: 5: 5

4.4.2.4 Alkylation with Epichlorohydrin

Another method of joining two dihydroxyacetophenone groups via a three carbon chain is to employ a cyclic compound which may act like a dihaloalkane on ring opening. Epichlorohydrin fulfils this role. The reaction scheme is as follows:



An important factor to note is the presence of two intermediates (14) and (15) which are the result of the opened epichlorohydrin able to undergo nucleophilic attack at either end. The final product, the dihydroxyacetophenone diether of epichlorohydrin (16), is reached as further nucleophilic attack occurs at the 'free' end of the 3 carbon chain.

The above reaction normally takes place in refluxing 4-methylpentan-2-one at approximately 129°C. Sonicating the reaction mixture with N-methylpyrrolidinone or dimethylformamide at this temperature presented no problems as these were high boiling point solvents. However it was expected that sonication would give no advantage to the 4-methylpentan-2-one reaction as this temperature was too close to the boiling point of the solvent and any cavitation bubbles formed would be filled with large amounts of solvent vapour. Lower temperatures resulted in minimal reaction.

After 4 hours the thermal reaction with refluxing 4-methylpentan-2-one resulted in 72% of the dihydroxyacetophenone diether of epichlorohydrin (16) with intermediates (11 and 12) present at 12.3% and 0.9% total product yield (see Table. 4.20 and Fig. 4.7).

Table. 4.20 - % Conversion of 2,6-dihydroxyacetophenone in 4-methylpentan-2-one under thermal reaction conditions.

TIME	**Starting Material**	**Intermed 1**	**Intermed 2**	**Final Product**
0 mins	-	-	-	-
15 mins	87.7%	3.4%	7.8%	1.0%
30 mins	76.6%	9.5%	7.8%	6.1%
45 mins	59.3%	15.5%	7.6%	17.6%
60 mins	57.3%	15.3%	5.8%	21.6%
90 mins	51.4%	15.8%	4.3%	28.5%
120 mins	37.7%	14.9%	1.9%	45.5%
180 mins	20.3%	14.0%	1.1%	64.5%
240 mins	14.7%	12.3%	0.9%	72.1%

Unexpectedly a competitive reaction is present within N-methylpyrrolidinone and dimethylformamide (see Tables Nos 4.21, 4.22 and Figs. 4.8, 4.9).

Table. 4.21 - % Conversion of 2,6-dihydroxyacetophenone in dimethylformamide under thermal reaction conditions.

TIME	**Starting Material**	**Intermed 1***	**Intermed 2**	**Final Product**
0 mins	-	-	-	-
15 mins	69.3%	5.9%	12.1%	12.8%
30 mins	49.6%	8.9%	10.4%	31.1%
45 mins	39.5%	9.8%	5.6%	43.9%
60 mins	40.7%	9.0%	3.1%	48.7%
90 mins	42.2%**	4.9%	1.0%	51.9%
120 mins	45.5%	1.7%	1.3%	51.6%
150 mins	53.5%	0.5%	1.8%	44.2%

* Not the same intermediate as that for 4-methylpentan-2-one

** As the reaction continues the amount of starting material appears to rise and the yield of final product falls. This is probably due to product decomposition.

Table. 4.22 - % Conversion of 2,6-dihydroxyacetophenone in N-methylpyrrolidinone under thermal reaction conditions.

TIME	**Starting Material**	**Intermed 1***	**Intermed 2**	**Final Product**
0 mins	-	-	-	-
15 mins	50.9%	12.4%	10.9%	25.8%
30 mins	-	-	-	-
45 mins	49.9%	6.0%	1.8%	42.2%
60 mins	48.6%	3.4%	2.3%	45.7%
90 mins	48.5%	1.9%	2.7%	47.0%
120 mins	60.0%**	0.8%	3.5%	35.5%

* Not the same intermediate as that for 4-methylpentan-2-one

** As the reaction continues the amount of starting material appears to rise and the yield of final product falls. This is probably due to product decomposition.

Epichlorohydrin alkylation of 2,6-dihydroxyacetophenone

Fig 4.7

Alkylation in 4-methylpentan-2-one

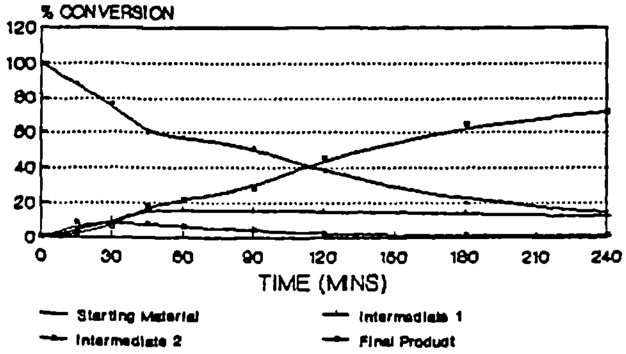


Fig 4.8

Alkylation in dimethylformamide

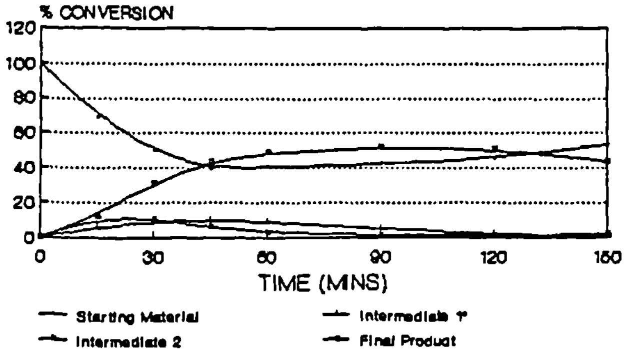
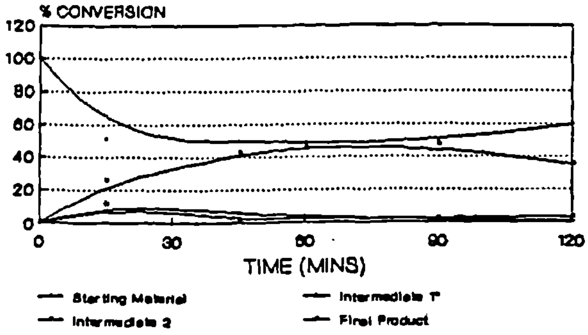


Fig 4.9

Alkylation in N-methylpyrrolidinone



INTERMEDIATE* NOT THE SAME AS THAT FOR 4-METHYLPENTAN-2-ONE

Similar product distributions and similar rates of reaction were obtained in these two solvents however the expected product yield was reduced to only a maximum 50%. Reaction in these solvents resulted in the production of a further intermediate not seen in 4-methylpentan-2-one. This intermediate reacted to give a second product which has not been identified.

Although these solvents have a lower vapour pressure than 4-methylpentan-2-one no advantage was seen over the thermal reaction when sonication was employed.

4.5CONCLUSION

If efficient cavitation is maintained the sonicated O-alkylation of 2,6-dimethylphenol may be enhanced by:-

1) A decrease in reaction temperature, lower temperatures support more efficient cavitation.

2) The most efficient alkylation is obtained with higher boiling, lower vapour pressure solvents. N-methylpyrrolidinone (NMP) and decalin, both high boiling solvents, exhibited a large degree of base size reduction thus indicating the presence of effective cavitation. However only NMP produced efficient O-alkylation. This suggests that in decalin a "close ion pair" must exist between the phenoxide ion and the base cation. The nature of the solvent must also be considered and polar aprotic solvents are more effective for O-alkylation.

3) The degree of association of the phenoxide ion with the base cation is important for efficient O-alkylation. The nature of the solvent must be considered and also the nature of the base cation. With smaller cations the degree of association is greater and the rate of alkylation is reduced. The rate of alkylation increases with base cation size increase. The

fastest rates were observed with the larger potassium cation.

4) A decrease in reaction volume produces an increase in reaction rate as the probability of reagent interaction and intensity of ultrasound per 1cm^3 is increased.

5) An increase in reagent concentration results in more effective alkylation due to an increased probability of reagent interaction plus increased cavitational collapse on or near the catalyst surface.

6) Finally an increase in power produces an increase in rate of alkylation as long as efficient cavitation is maintained.

CHAPTER 5

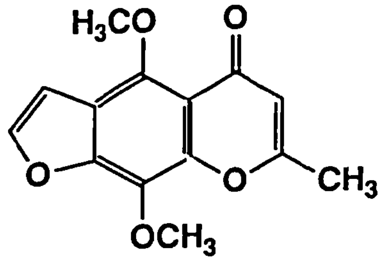
SONOCHEMICALLY ASSISTED O-ALKYLATION OF 5-HYDROXYCHROMONES

5.0 O-ALKYLATION OF 5-HYDROXYCHROMONES

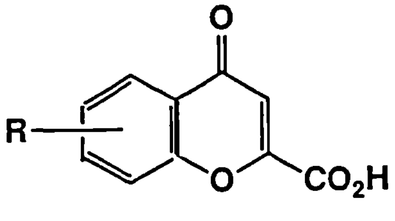
5.1 INTRODUCTION

People suffering from allergic asthma develop sensitivity to grass pollens, hair and house dust. These allergy causing factors are known as allergens or antigens and their presence often results in an asthma attack. An asthma attack normally results in a reduction of the amount of air passing through the lungs due to a widespread narrowing of lung airways caused by either a contraction of circular muscle fibres, inflammation and swelling of airway lining or the excess secretion of mucus in the lungs. To combat such attacks bronchodilator drugs, which reduce constriction in the lung airways, are used at the onset of an attack.

In the search for new bronchodilator drugs Fisons, or Bengers laboratories as it was known at the time, synthesised analogues of Khellin (17), which is a known bronchodilator present as an active constituent in plants with this property[61]. In order to make the new molecules water soluble, allowing inhalation through an aerosol spray, a series of chromones with a water soluble carboxylic acid functionality (18) were produced.

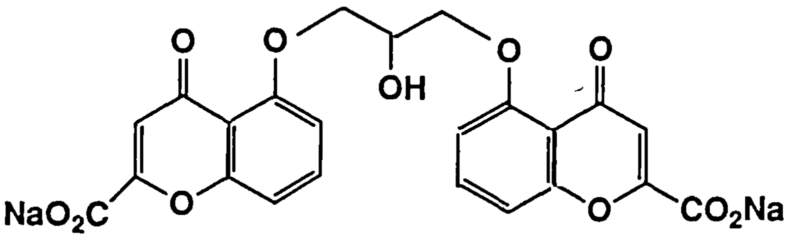


(17)



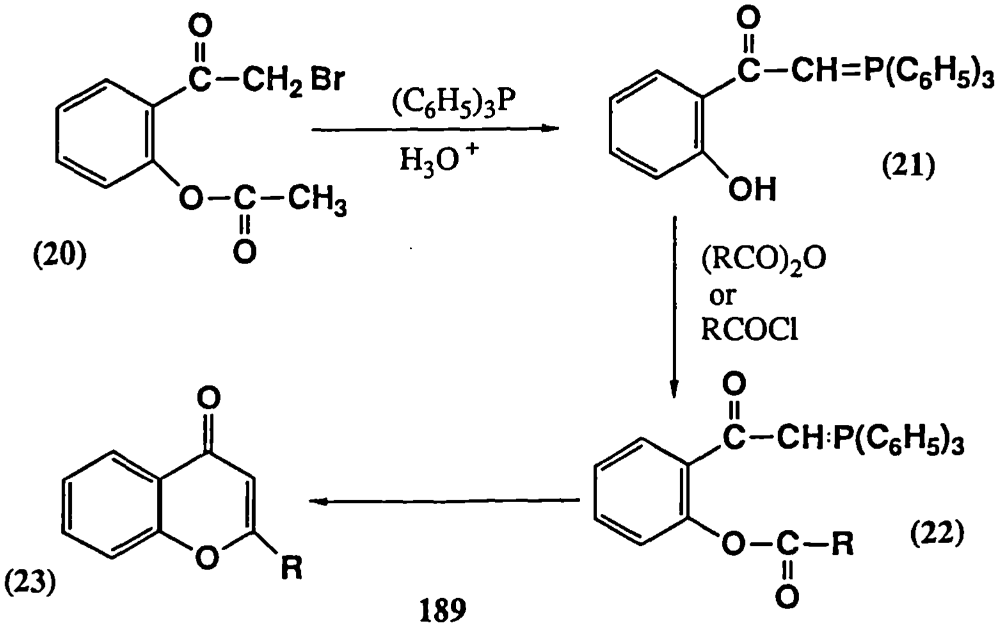
(18)

Although these products were found to be inactive as bronchodilators they provided some inhibition to the action of allergens and so prevented the initiation of an asthma attack. The most active substrate contained a 5-alkoxy functionality but protection against asthma attack lasted only 10 minutes. The development of a bis-chromone resulted in the marketing of sodium chromoglycate (Intal) (19) with a much extended period of allergen inhibition.



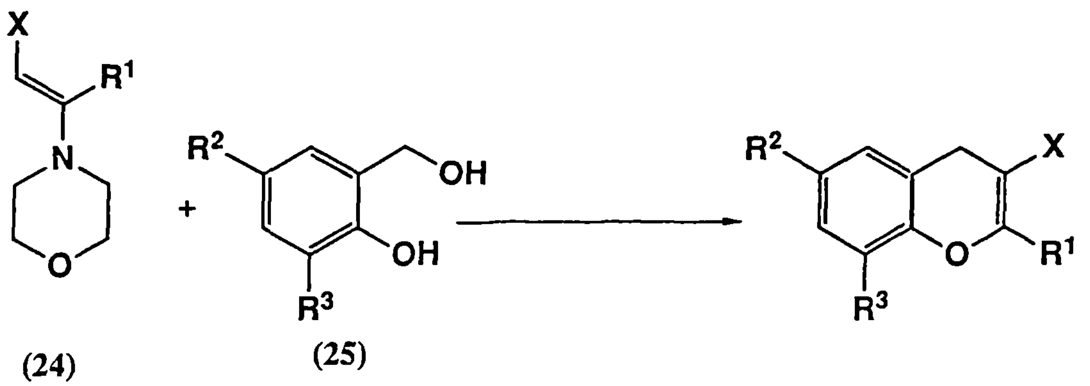
(19)

Chromone and chromone-like substrates are therefore much in demand in the pharmaceutical industry as anti-asthma drugs. Their syntheses often require several steps and so the search is on for more simple routes. Hercouet and Le Corre[62] described a simple synthesis of chromones from o-hydroxyphenacylidene triphenylphosphorane. The reaction scheme is as follows.



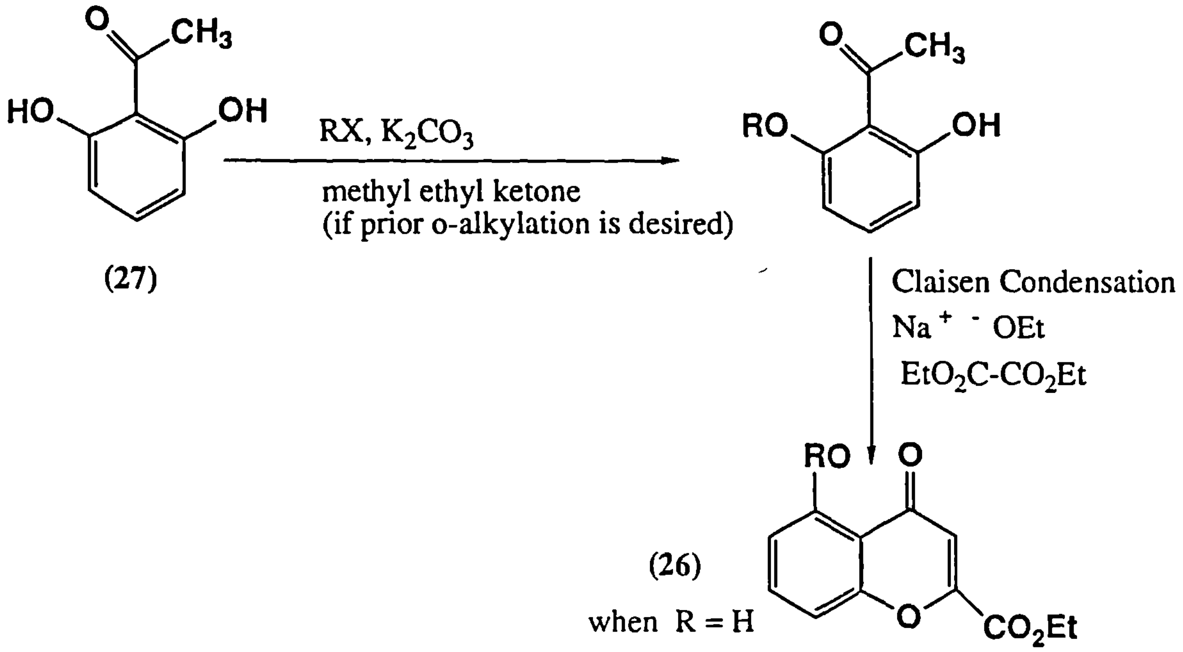
Triphenylphosphine is reacted with o-acetoxyphenacyl bromide (20) to give phosphorane (21) which in turn is reacted with a carboxylic acid chloride or anhydride to give another phosphorane (22). This phosphorane undergoes spontaneous intramolecular rearrangement to give the chromone (23).

Rene[63] introduced a new approach to the synthesis of functionalised 4H-chromenes (containing a similar backbone to chromones).



The use of functionalised enamines (24) with electron withdrawing groups in a β position will react with substituted o-hydroxybenzyl alcohols (25) in refluxing acetic anhydride to produce functionalised 4H-chromones.

Previous work in our laboratories resulted in the synthesis of 5-hydroxy-4-oxo-4H-benzopyran-2-carboxylic acid ethyl ester (26) via the reaction of sodium ethoxide with 2,6-dihydroxyacetophenone (27) and subsequent Claisen condensation with diethyl oxalate[64]. If an alkoxy product is desired addition of an alkyl halide and base prior to Claisen condensation results in the formation of the O-alkylated benzopyran product.



(27)

(26)
when R = H

Direct O-alkylation of 5-hydroxy-4-oxo-benzopyranones (5-hydroxychromones) is not easily achieved due to the hydrogen bonding between the hydroxide and the adjacent carbonyl grouping reducing the nucleophilicity of the resulting phenoxide.

One method of avoiding direct O-alkylation of the hydroxy-4-oxo-4H-benzopyranone (hydroxychromone) was demonstrated by Appleton[65]. The O-alkylated chromone-2-carboxylic acid was produced by the simple alkylation of the precursor 2,6-dihydroxyacetophenone with subsequent hydrolysis and Claisen condensation producing the required chromone molecule.

Direct O-alkylation of hydroxychromones can prove to be extremely difficult. Naik et al[66] reported that methoxylation of 5-hydroxy-2-methylchromone with methyl iodide required reflux for 24 hours in dry acetone with a further addition of methyl iodide and further 24 hour reflux to produce 5-methoxy-2-methylchromone.

More efficient methods of achieving direct O-alkylation of hydroxychromones are therefore necessary.

Ultrasound has been shown to be efficient under heterogeneous reaction conditions and in the O-alkylation of hindered phenols (see earlier Chapter 4). When applied to the O-alkylation of the 5-hydroxychromone system excellent results were obtained[64].

The O-alkylation of 5-hydroxychromone-2-carboxylic acid ethyl ester by iodomethane in the presence of potassium carbonate and probe sonication produced 88.7% of the 5-methoxychromone-2-carboxylic acid ethyl ester within 30 minutes at 65°C compared to 28% under thermal reaction conditions[67]. Allyl, benzyl and propyl halides also give much improved yields of O-alkylated product under sonicated reaction conditions.

5.2 EXPERIMENTAL CONDITIONS

The reactions were performed as stated in section 2.3.1. Both the thermal and sonicated reactions were repeated with 2-bromobutane, 1-iodopropane and 2-bromopropane.

5.3 ANALYSIS CONDITIONS

HPLC CONDITIONS

The equipment employed was the Hewlett Packard 1090L (series 1) with a Hewlett Packard filter photometric detector with Hewlett Packard 3396 integrator using the INET command system.

HPLC Conditions for the analysis of the alkylation of 5-hydroxychromone-2-carboxylic acid ethyl ester

A two solvent system was employed.

Solvent A - 50cm^3 of stock acetate buffer (see earlier) diluted to 1000cm^3 with HPLC grade water.

Solvent B - 50cm^3 stock acetate buffer diluted to 700cm^3 with HPLC grade acetonitrile and then diluted to 1000cm^3 with HPLC grade water.

A 15cm ODS general purpose column was employed and the analysis conditions were as follows:

Flow Rate	1.5cm^3/ min
Maximum Pressure	400 bar
Minimum Pressure	50 bar
Oven Temperature	45°C
Attenuation	6
Wavelength	245nm

At time = 0	% Solvent B = 25
Time = 3	%B = 25
Time = 15	%B = 70
Time = 25	%B = 90
Time = 30	%B = 95
Time = 35	%B = 70
Time = 37	%B = 25

5.4 RESULTS/ DISCUSSION

In an attempt to compare the non-conventional techniques of phase transfer catalysis and ultrasound a joint effort between Coventry Polytechnic and the University of Paris-Sud was established.

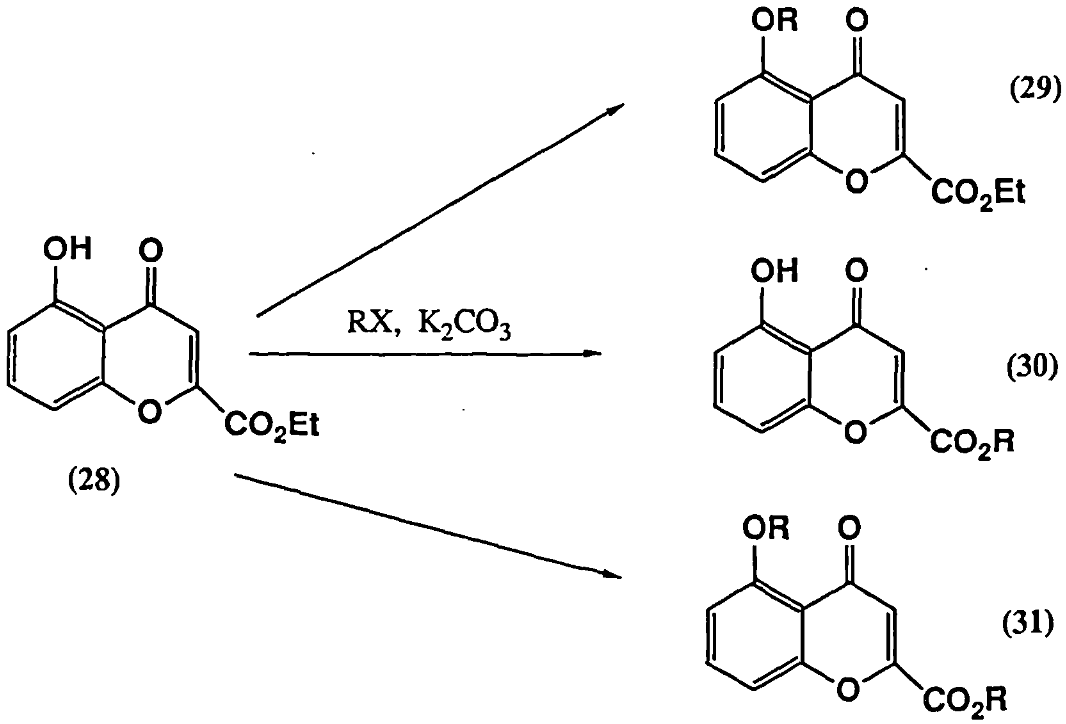
Phase Transfer Catalysis

Phase transfer catalysis is employed within two phase reactions where a catalytic amount of a phase transfer agent is introduced so that one of the reagents may be brought into contact with another reagent in a different phase.

One example of a phase transfer reaction can be given in the cyanide displacement of a halide ion from an alkyl halide[68]. A 2 phase mixture of an alkyl halide and aqueous sodium cyanide does not result in cyanoalkane formation even after several hours of heating and stirring. The addition of a phase transfer catalyst, a quaternary ammonium salt, enhances the exchange to give the corresponding cyanoalkane within 1-2 hours. Several phase transfer reagents are available and include quaternary ammonium salts, crown ethers and dialkylpolyethylene oxides.

Sonication has been shown to produce efficient mixing due to microstreaming (see earlier). More effective mass transfer is present and thus a more efficient phase transfer occurs. Phase transfer catalysis in the absence of solvent has been investigated by Bram et al[69] and the production of esters and ethers via alkylation of acetates, carboxylates and alkoxide ions has been examined. The phase transfer O-alkylation of aryl phenols to produce aromatic ethers[70] in the absence of solvent has also been investigated. High yields of the aromatic ether were obtained from a reaction of phenoxide ion with the alkyl halide in the presence of potassium hydroxide base and phase transfer catalyst Aliquat 336. Aliquat 336 consists of $(C_8H_{17})_3NCH_3Cl$ and is one of the most efficient phase transfer catalysts available. Absence of solvent reduces the overall reaction costs and reaction 'work up' consists of simple filtration of the final reaction mixture through Fluorosil, which removes the phase transfer catalyst, and product elution with diethyl ether.

The alkylation of 5-hydroxychromone-2-carboxylic acid ethyl ester (28) with 1-bromobutane and 2-bromobutane was to be attempted and the resulting product distributions examined. With highly reactive alkyl halides such as allyl bromide and benzyl bromide the only product observed on alkylation of 5-hydroxychromone-2-carboxylic acid ethyl ester (28) is an O-alkylated product (29). Alkyl halides such as 1-iodopropane also produce the same results. The product distribution is altered when less reactive and/ or more hindered alkyl halides, such as 1-bromobutane, are employed. In these cases O-alkylation is less facile resulting in a widened product distribution. A transesterified product (30) and/or the disubstituted O-alkylated transesterified product (31) are now observed.



The alkylation products of 5-hydroxychromone-2-carboxylic acid ethyl ester with 1-bromo and 2-bromobutane under phase transfer, sonicated and thermal conditions were compared[71].

5.4.1 1-bromobutane (see Table. 5.1, 5.3 and Fig. 5.1)

The O-alkylation of 5-hydroxychromone-2-carboxylic acid ethyl ester at 120°C after 5 hours under phase transfer conditions in the presence of Aliquat 336 resulted in 85% of the disubstituted O-alkylated and transesterified product (31), *i.e.* the 5-butoxychromone-2-carboxylic acid butyl ester, employing an initial 1:2 ratio of chromone:alkyl halide. No indication of the reaction pathway was given until the initial reagent ratios were altered to a 1:1 ratio of chromone:alkyl halide and then it could be seen that the reaction pathway utilised an O-alkylated intermediate (29), *i.e* the 5-butoxychromone-2-carboxylic acid ethyl ester. O-alkylation was the preferred route of reaction.

Table. 5.1 - A comparison of two techniques:- Product distribution of 5-hydroxychromone-2-carboxylic acid ethyl ester alkylation after 5 hours.

Phase Transfer Catalysis with Aliquat 336					
Alkyl halide	**Temp**	**Starting Material**	**O-alkyl Product***	**Trans Product***	**Disubst Product***
1-bromo	120°C	15.0%	-	-	85.0%
1-bromo+	120°C	26.0%	23.0%	3.0%	48.0%
2-bromo	120°C	76.0%	-	24.0%	-

+ - Initial reagents altered to a 1:1 ratio

* - Starting Material - 5-hydroxychromone-2-carboxylic acid ethyl ester
O-alkylated Product - 5-alkoxychromone-2-carboxylic acid ethyl ester
Transesterified Product - 5-hydroxychromone-2-carboxylic acid alkyl ester
Disubstituted Product - 5-alkoxychromone-2-carboxylic acid alkyl ester

Table. 5.2 - A comparison of two techniques:- Product distribution of 5-hydroxychromone-2-carboxylic acid ethyl ester alkylation after 5 hours.

Phase Transfer Catalysis with 50% Crown Ether					
Alkyl halide	**Temp**	**Starting Material**	**O-alkyl Product***	**Trans Product***	**Disubst Product***
2-bromo	60°C	70.0%	30.0%	-	-
2-bromo	80°C	12.0%	52.0%	17.0%	19.0%

* - Starting Material	- 5-hydroxychromone-2-carboxylic acid ethyl ester
O-alkylated Product	- 5-alkoxychromone-2-carboxylic acid ethyl ester
Transesterified Product	- 5-hydroxychromone-2-carboxylic acid alkyl ester
Disubstituted Product	- 5-alkoxychromone-2-carboxylic acid alkyl ester

The major product observed under sonicated and thermal reaction conditions was the single O-alkylated product (see later Table. 5.3). This may be simply due to the lower temperatures involved, 65°C, when compared to the phase transfer catalysis temperatures of 120°C, resulting in a slower overall reaction rate.

5.4.2 2-bromobutane (see Tables. 5.1,5.2,5.3 and Fig. 5.2)

Phase transfer catalysis produced more interesting results with 2-bromobutane. It seemed that only transesterification (30), to give the 5-hydroxychromone-2-carboxylic acid butyl ester, was present at 120°C with no evidence of O-alkylation when Aliquat 336 was employed. 50% conversion of the starting material was obtained after 5 hours reaction time. With crown ether at 60°C only O-alkylated product was observed, although some transesterification was obtained at the higher temperature of 80°C.

Preliminary results under thermal and sonicated reaction conditions indicated a slight preference for O-alkylation to finally give the disubstituted O-alkylated transesterified

Fig 5.1 - Comparison of 2 alkylation techniques for the alkylation of 5-hydroxychromone-2-carboxylic acid ethyl ester with 1-bromobutane

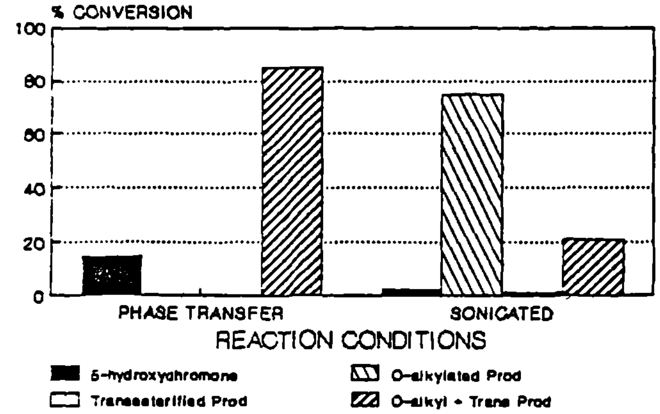


Fig 5.2 - Comparison of techniques for the alkylation of 5-hydroxychromone-2-carboxylic acid ethyl ester with 2-bromobutane

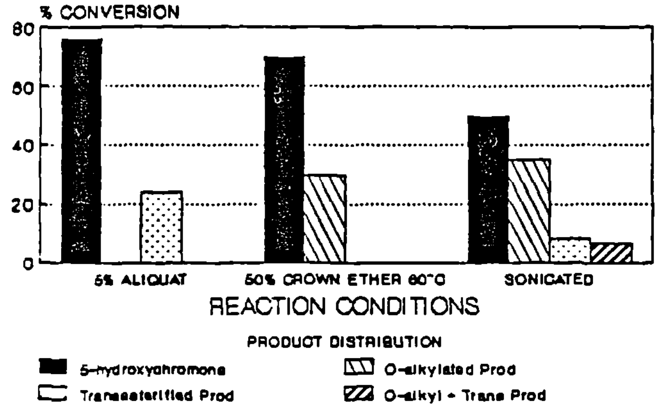
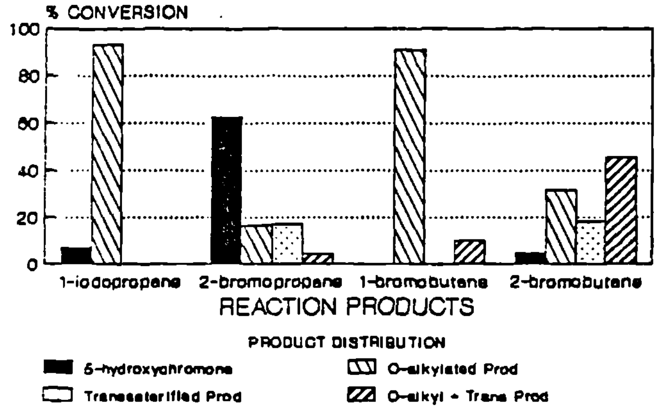


Fig 5.3 - Comparison of the product distribution of the alkylation of 5-hydroxychromone-2-carboxylic acid ethyl ester with various alkyl halides



product (see Table. 5.3). Some transesterification was also in evidence. Approximately 95% conversion of the starting material was observed after 5 hours reaction time with a wider product distribution than the less hindered 1-bromobutane.

Table. 5.3 - A comparison of two techniques:- Product distribution of 5-hydroxychromone-2-carboxylic acid ethyl ester alkylation after 5 hours.

Product Distribution					
Alkyl halide	**Temp**	**Starting Material**	**O-alkyl Product***	**Trans Product***	**Disubst Product***
1-bromo	65°C	2.8%	74.8%	1.1%	21.3%
1-bromo (th)	65°C	16.3%	78.1%	1.7%	3.9%
2-bromo (us)	65°C	49.8%	35.1%	8.5%	6.6%
2-bromo (th)+	65°C	38.7%	41.1%	14.6%	5.5%

+ - After 4 hours reaction only
* - Starting Material - 5-hydroxychromone-2-carboxylic acid ethyl ester
O-alkylated Product - 5-alkoxychromone-2-carboxylic acid ethyl ester
Transesterified Product - 5-hydroxychromone-2-carboxylic acid alkyl ester
Disubstituted Product - 5-alkoxychromone-2-carboxylic acid alkyl ester
Non derivatised GLC results employed

5.4.3 1-iodopropane (see Table. 5.4 and Fig. 5.4)

The sonicated alkylation of 5-hydroxychromone-2-carboxylic acid ethyl ester with 1-iodopropane was monitored. The use of HPLC and GLC/Mass spectroscopy for product identification was employed as this work was completed at Fisons Pharmaceuticals. Fisons have a well established method for product identification encompassing many years experience and all products and side products have been very well characterised.

Fig 5.4 - **Alkylation of 5-hydroxychromone-2-carboxylic acid ethyl ester with 1-iodopropane**

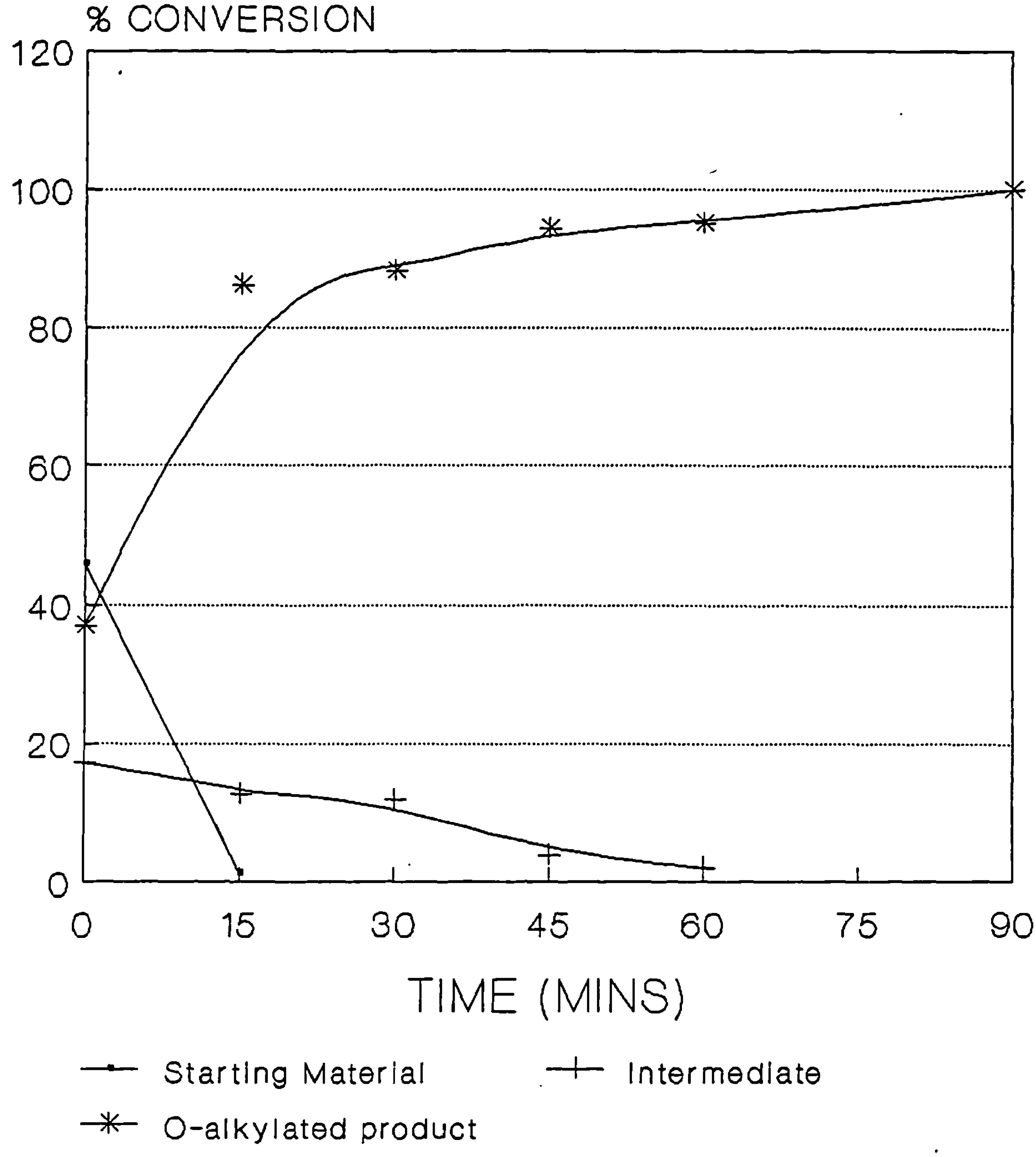


Table. 5.4 - % Conversion of the sonicated alkylation of 5-hydroxychromone-2-carboxylic acid ethyl ester with 1-iodopropane.

Product Distribution			
Time	Starting Material	Intermediate	Propoxy-chromone
0 mins	45.8%	17.2%	37.0%
15 mins	1.2%	12.7%	86.0%
30 mins	-	11.8%	88.2%
45 mins	-	3.9%	94.2%
60 mins	-	2.0%	95.1%
90 mins	-	-	100.00%

The starting material was quickly depleted within 30 minutes and there was a short lived substance formed which disappeared after 90 minutes. The final product was formed very quickly and reached over 93% conversion. Some degradation, approximately 3%, of the starting material 5-hydroxychromone-2-carboxylic acid ethyl ester to its precursor 2,6-dihydroxyacetophenone occurred. No transesterification was observed and the major product was identified as the O-alkylated 5-propoxychromone-2-carboxylic acid ethyl ester by GC/ Mass spectroscopy.

5.4.4 2-bromopropane (Table. 5.5)

The results obtained via GC/ Mass spectroscopic analysis, at Fisons, from the reaction of 5-hydroxychromone-2-carboxylic acid ethyl ester with 2-bromopropane after 5 hours sonication were as follows:-

Starting Material	5-hydroxychromone-2-carboxylic acid ethyl ester	- 62.4%
O-alkylated Product	5-propoxychromone-2-carboxylic acid ethyl ester	- 16.6%

Transesterified Product	5-hydroxychromone-2-carboxylic acid propyl ester	- 17.0%
Disubstituted Product	5-propoxychromone-2-carboxylic acid propyl ester	- 4.0%

O-alkylation and transesterification had similar product yields suggesting a similarity in rates of reaction of these two pathways for nucleophilic attack by a slightly hindered alkyl halide.

Table. 5.5 - A summary of the reaction products after 5 hours of the alkylation of 5-hydroxychromone-2-carboxylic acid ethyl ester with a series of alkyl halides.

	Product Distribution			
Alkyl Halide	**Starting Material***	**O-alkyl Product***	**Trans Product***	**Disubst Product***
1-iodoprop (us)	7.0%	93.0%	-	-
2-bromopro (us)	62.4%	16.6%	17.0%	4.0%
1-bromobut (us)	-	90.0%	-	9.7%
2-bromobut (us)	5.0%	31.3%	18.2%	45.5%

* - Starting Material	- 5-hydroxychromone-2-carboxylic acid ethyl ester
O-alkylated Product	- 5-alkoxychromone-2-carboxylic acid ethyl ester
Transesterified Product	- 5-hydroxychromone-2-carboxylic acid alkyl ester
Disubstituted Product	- 5-alkoxychromone-2-carboxylic acid alkyl ester

5.5 CONCLUSION

The alkylation products of 5-hydroxychromone-2-carboxylic acid ethyl ester altered depending upon the technique employed.

1) Alkylation with 1-bromobutane in the presence of a phase transfer catalyst produced a disubstituted product via an O-alkylation reaction pathway. However with ultrasound and thermal reaction conditions an O-alkylated product was obtained which did not go on to form the disubstituted product, however lower reaction temperatures were employed.

2) Alkylation with 2-bromobutane under sonicated or thermal reaction conditions produced the O-alkylated product which continued to form the disubstituted product. In the presence of a phase transfer catalyst the final product may be altered by changing the catalyst employed. Aliquat 336 resulted in a transesterified product but Crown ether produced an O-alkylated product.

Final reaction products are dependant upon the technique employed. Sonicated and thermal reaction conditions preferred the O-alkylation reaction pathway but transesterification may be induced by phase transfer catalysis.

CHAPTER 6

SONOCHEMICAL DEHYDROGENATION OF TETRAHYDRONAPHTHALENE

6.0 DEHYDROGENATION OF TETRAHYDRONAPHTHALENE

6.1 INTRODUCTION

Hydrogenation is widespread throughout all aspects of chemistry research laboratories as well as large scale chemical plants. It is a very important synthetic route to many organic compounds therefore any enhancement in the performance of a hydrogenation reaction would be very advantageous.

Several investigations into hydrogenation rate enhancement by sonication have been documented. Boudjouk and Han[72] refer to the hydrogenation system of 10% palladium on activated carbon catalyst with formic acid as a hydrogen donor. In their investigations sonic waves enhance the hydrogenation rate. The sonicated reaction is complete within 1 hour compared to the thermal reaction which only goes to greater than 70% conversion within 1 hour.

Large scale hydrogenations are employed by many chemical companies, the hydrogenation of vegetable oils to produce margarines being a well known example.

Moulton and Koritala[73] introduced the results obtained on application of ultrasonic energy to the hydrogenation of soyabean oil in the presence of copper chromite or nickel catalyst.

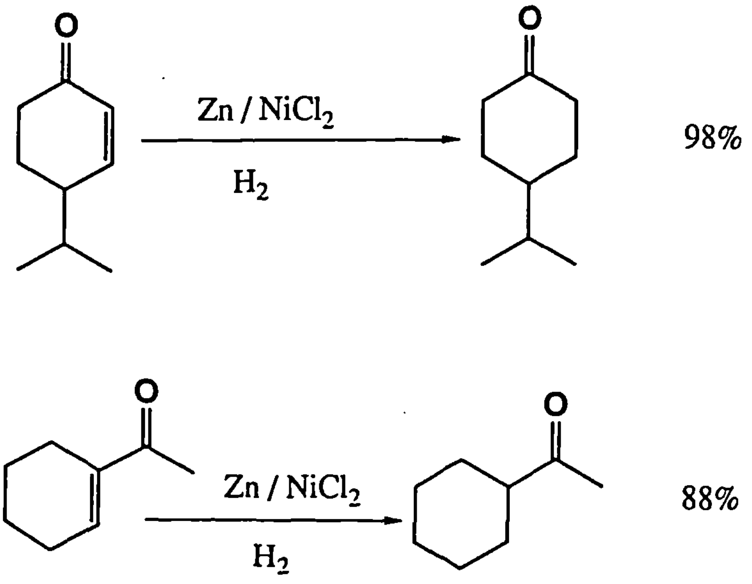
In the presence of ultrasound 87% of linolenate was hydrogenated in 9 seconds with 1% copper chromite and 77% with 0.025% nickel catalyst at 181°C under 115 psig Hydrogen. In the absence of ultrasound only 59% hydrogenation was achieved in 240 seconds with copper chromite at 198°C and 500 psig Hydrogen and 68% hydrogenation occurred in 480 seconds with nickel catalyst at 200°C and 115 psig Hydrogen. Ultrasound therefore appears to enhance the performance of hydrogenation catalysts.

The hydrogenation of unsaturated hydrocarbons using nickel powder as the catalyst is an unusual system. It was shown that in the presence of ultrasound the nickel powder is activated enough, due to particle size reduction and fresh surface area exposure, to induce hydrogenation at room temperature and pressure[21].

Suslick and Casadonte[51] report that upon sonication of nickel powder an increase in hydrogenation rate is observed. Hydrogenation of alkenes is usually not possible when using nickel as the catalyst, for example rapid stirring under a hydrogen atmosphere for 2×10^4 minutes does not result in alkane formation.

Prior sonication of the catalyst (optimum time approximately 1 hour) results in 1-nonene being hydrogenated. Similar rates are observed for the hydrogenation of 1-decene, cis-5-decene, trans-5-decene, cyclooctene and cyclohexene. Reduction of ketones or aldehydes does not occur (thus making nickel a more selective catalyst and far easier to prepare than other well known catalysts).

Zinc metal is activated by nickel chloride and used in the hydrogenation of α,β-unsaturated carbonyl compounds[74] (32).



(32)

In the presence of water and ultrasonic irradiation, to increase reaction rate and aid completion, it was noted that hydrogenation occurs first at the unsaturated double bond and only then at the carbonyl bond.

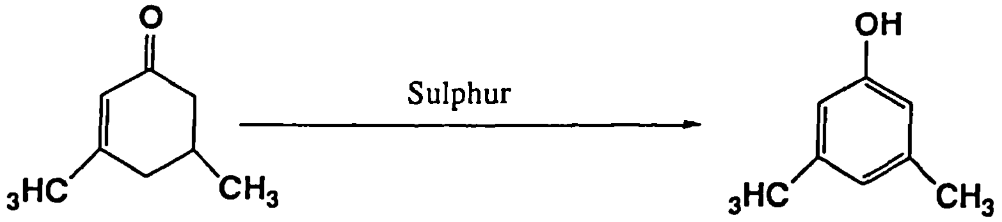
Activation of the zinc metal by other methods does not provide the desired result.

Although sonicated hydrogenation has been very well exploited by the research chemist the reverse of this reaction is not as well known. Dehydrogenation offers a route to many organic molecules. Easily achieved it is a valuable procedure in organic synthesis.

Nowadays catalytic dehydrogenation by the use of activated catalysts, such as palladium, platinum and nickel, is the first method to come to mind when considering a dehydrogenation reaction[75]. However dehydrogenation can be achieved through a variety of procedures.

Dehydrogenation in the presence of sulphur or selenium is one route to obtaining the desired substances. Sulphur dehydrogenation is usually performed at temperatures between 200°C and 250°C. The exact mechanism of dehydrogenation is not known however it certainly involves the abstraction of hydrogen ions from the substrate leaving a double bond. The hydrogen ions go on to react with the sulphur to give the odorous hydrogen sulphide gas, one disadvantage of this procedure.

A simple example of sulphur dehydrogenation is given by Horning[76] where the dehydrogenation of 3,5-dimethylcyclohex-1-one (33) resulted in the formation of 3,5-dimethylphenol (34).

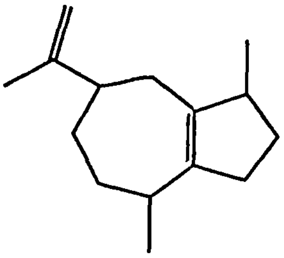


(33) (34)

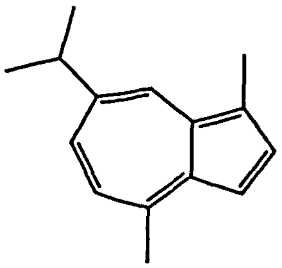
Selenium requires higher temperatures of 250°C to 300°C to achieve dehydrogenation. Hydrogen selenide, and other selenides, are often by-products and are even more toxic than the sulphur analogues.

With the above procedures obvious disadvantages are present. Although dehydrogenation is achieved it is not very selective and many functional groups are also dehydrogenated. Often dehydration of secondary and tertiary alcohols also occurs.

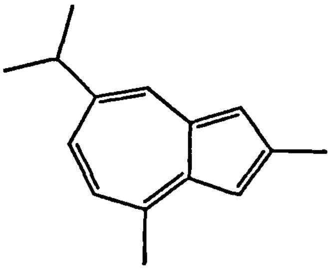
Due to the high temperatures employed product rearrangements and isomerisations are also possible. One example of product rearrangement was shown by House and Orchin[77]. The dehydrogenation of guaiene (35) in the presence of sulphur resulted in the product known as S-guaiazulene (36). Dehydrogenation of guaiene in the presence of selenium, at higher temperatures, resulted in the product known as Se-guaiazulene (37). Lowering the temperature of selenium dehydrogenation by 20°C resulted in more formation of S-guaiazulene which isomerised to Se-guaiazulene only in the presence of selenium and at higher temperatures.



(35)

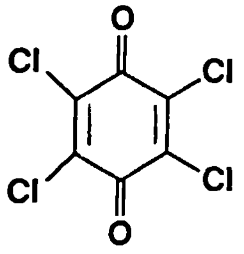


(36)

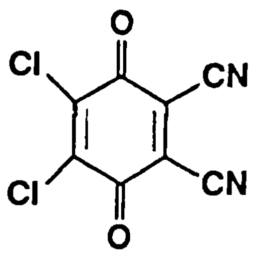


(37)

Dehydrogenation may also be achieved by the use of quinones with electron withdrawing substituents. Chloranil[78] (38) is often employed with cyclohexene systems which are readily dehydrogenated to the corresponding benzene system. More reactive quinones such as dichlorodicyanoquinone (39) are necessary for more difficult dehydrogenations.



(38)



(39)

Leffingwell and Bluhm[79] investigated aromatisations of certain simple cyclohexene systems in the presence of manganese dioxide. In the presence of excess activated manganese dioxide the dehydrogenation of certain cyclohexene aldehydes and ketones, to their corresponding aromatic derivatives, is possible. Kimura and Fujita[80] report the simple sonochemical activation of manganese dioxide, via the use of a sonic cleaning bath, and the subsequent selective dehydrogenation of cinnamyl alcohol to cinnamyl aldehyde.

The study of catalytic dehydrogenation was pioneered by Linstead in the late 1930's. The dehydrogenation of a wide range of substrates by the use of palladium, platinum and nickel catalysts was examined. The most active catalyst for the dehydrogenation of hydronaphthalenes[81] was shown to be a palladium on activated charcoal mixture resulting in the formation of naphthalenes from tetralins and dihydronaphthalenes. The formation of naphthols from hydroaromatic alcohols and ketones[82] and also the dehydrogenation of terpenes and terpene ketones[83] was also explored. The use of catalysts offered more specific dehydrogenations and less rearrangement/ isomerisation due to the lower temperatures at which dehydrogenation was now made possible.

New routes to dehydrogenation are always being sought. The effect of sonication on dehydrogenation has at this present time remained unreported. Hydrogenation on the other hand has been investigated and it is surprising that the reverse of this reaction has not received much interest. One quote dedicated to sonochemical dehydrogenation can be found in a Boudjouk paper[72] concentrating on the sonochemical catalytic hydrogenation of alkenes in the presence of a formic acid hydrogen transfer agent. This result was obtained when an ethanolic solution of cyclohexene, sonicated in the presence of formic acid and palladium/ carbon catalyst produced cyclohexene and benzene in a 2:1 ratio.

The following series of experiments was established in an effort to determine whether power ultrasound can assist catalytic sonochemical dehydrogenation.

6.2 EXPERIMENTAL CONDITIONS

Comparison of thermal conditions with sonicated conditions

The standard experimental conditions were followed as outlined in section 2.4.1.

Thermal reactions were repeated at 180°C and 200°C whilst the sonicated reaction at 200°C was thought to be unnecessary as sonication already showed significant rate enhancement at the lower temperatures.

Addition of fresh catalyst

The standard experimental conditions were followed as outlined in section 2.4.1. The reaction was stirred for 4 hours and then a further 0.1g of fresh 3% Pd/C catalyst was added. Stirring was continued for a further 4 hours and after 8 hours reaction 0.05g of fresh catalyst was added once again. Aliquots were withdrawn half hourly and filtered through silica to remove the solid catalyst. Samples were analysed by GLC as the reaction progressed.

Thermal reaction followed by activation with sonication

The standard experimental conditions were followed as outlined in section 2.4.1. The reaction was stirred for 4.5 hours and the flask was then slightly cooled, in order that the reaction temperature was kept at 200°C even after sonication. Probe sonication was applied via a 0.6cm diameter tip horn at 6% power output (setting 2.5) with the Sonics and Materials equipment. The reaction was sonicated for a further 2.5 hours. Aliquots were withdrawn half hourly and then hourly, filtered through silica and analysed by GLC.

Increase in applied power

The standard experimental conditions were followed as outlined in section 2.4.1. However the power applied was altered as the probe sonication was altered from 20% power output (setting 4) to 32% power output (setting 6) employing the Sonics and Materials equipment.

Pulsed Power

The standard experimental conditions were followed as outlined in section 2.4.1.

The experiment was repeated at 12% power output (setting 5) with a 50% and also a 10% duty/pulse cycle.

Solvent Alterations

The standard experimental conditions were followed as outlined in section 2.4.1.

The sonicated and thermal reactions were repeated altering the solvent to triethyleneglycol dimethyl ether (triglyme), triethyleneglycol (trigol) and diethyleneglycol dimethyl ether (diglyme).

6.3 ANALYSIS CONDITIONS

GLC CONDITIONS

The Perkin Elmer F33 gas chromatograph with a Shimadzu integrator was employed using a 5% carbowax packed stainless steel column (length 2m, diameter 0.5cm).

Column Temperature	210°C
Injector/Detector Temperature	250°C
Run Time	10 mins

Retention Times

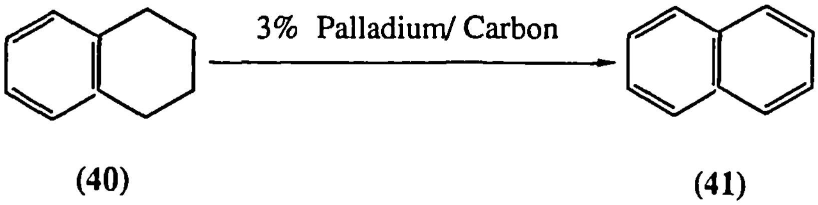
Diethyleneglycol (digol)	11.26 mins
Tetrahydronaphthalene	3.48 mins
Naphthalene	5.73 mins

Diethyleneglycol dimethyl ether (diglyme)	1.70 mins
Tetrahydronaphthalene	3.23 mins
Naphthalene	5.40 mins
Triethyleneglycol (trigol)	does not appear within run time
Tetrahydronaphthalene	3.04 mins
Naphthalene	5.04 mins

Triethyleneglycol dimethyl ether (triglyme)	9.43 mins
Tetrahydronaphthalene	6.84 mins
Naphthalene	11.41 mins

6.4 RESULTS/ DISCUSSION

Aromatization is more easily achieved if there are double bonds already present within the single ring system or if the ring is fused to another aromatic ring. Such is the case for tetrahydronaphthalene (40). It is expected that catalytic aromatization of tetrahydronaphthalene should result in the formation of the fully aromatic naphthalene (41).



Thermal catalytic dehydrogenations normally require high temperatures, approximately 280 - 300°C. After a time the catalyst becomes denatured and second additions of activated catalyst are often required in order to bring the reaction to completion. It is thought that the ability of ultrasound to activate catalysts[51] and reduce the temperature required for reaction may prove extremely useful in this type of reaction.

On comparing thermal dehydrogenation with the corresponding sonicated reaction (see Table. 6.1 and Fig. 6.1) it was noted that thermally there was no appreciable dehydrogenation occurring below 200°C. It should be also noted that no dehydrogenation products are present in the absence of palladium on activated carbon catalyst.

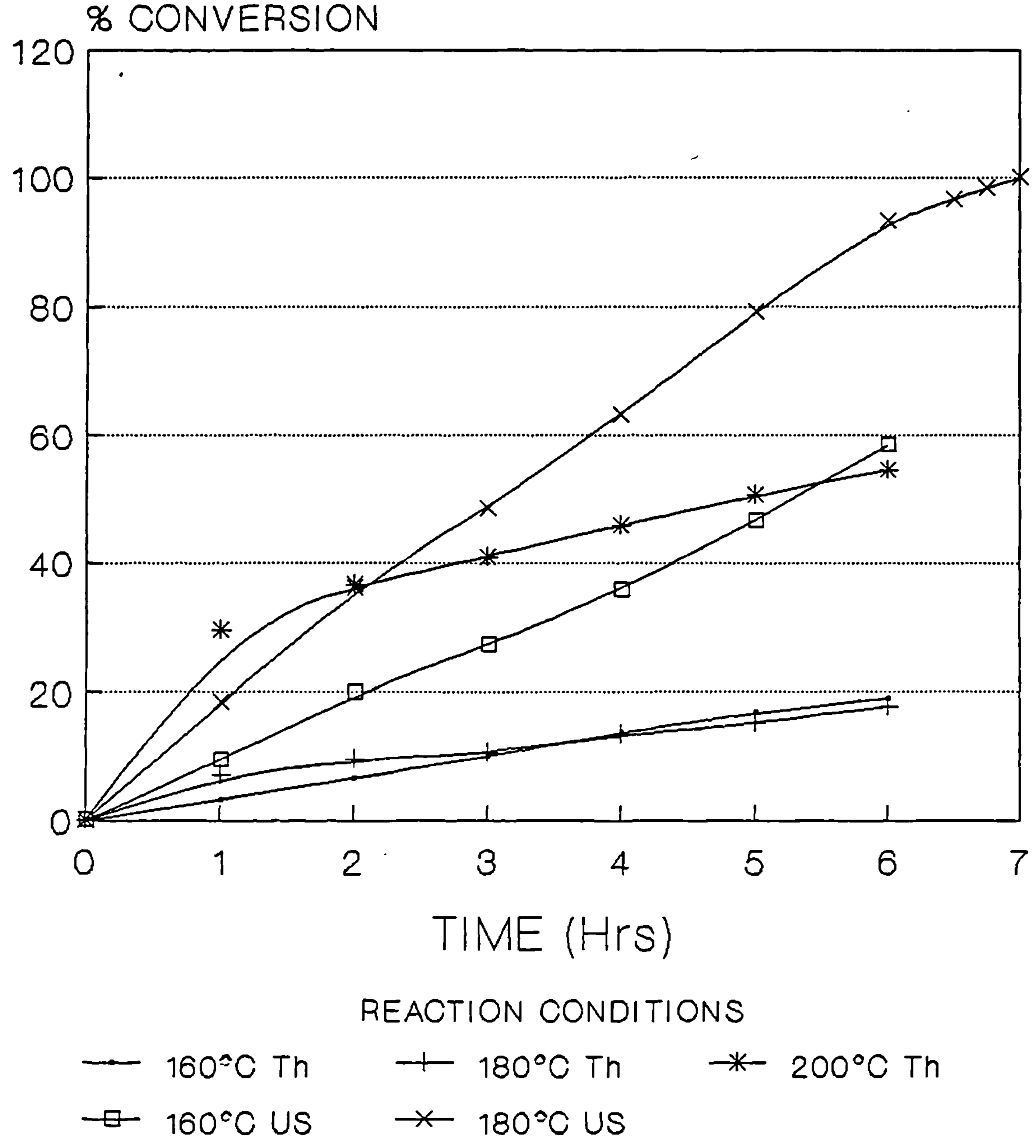
Table. 6.1 - % Conversion of tetrahydronaphthalene with respect to temperature and mode of reaction.

	THERMAL			SONICATED	
TIME	160°C	180°C	200°C	160°C	180°C
1.0 hour	3.26%	7.10%	29.5%	9.4%	18.4%
2.0 hours	6.50%	9.5%	36.6%	19.9%	36.1%
3.0 hours	10.10%	10.6%	40.9%	27.2%	48.5%
4.0 hours	13.90%	13.5%	45.9%	35.7%	63.3%
5.0 hours	16.90%	15.2%	50.6%	46.5%	79.3%
6.0 hours	19.00%	17.8%	54.6%	58.4%	93.3%
6.5 hours	-	-	-	-	96.7%
6.75 hours	-	-	-	-	98.5%
7.0 hours	-	-	-	-	100.0%

At 200°C the initial rate of the thermal reaction was fast but then began to tail off, possibly a result of the active sites on the catalyst becoming filled coupled with a slow removal of products. The sonicated reactions did not exhibit this reduction in reaction rate and were fairly constant throughout. This could be attributed to the continuing availability of catalyst active sites. One of the features of heterogeneous sonicated reactions is the constant exposure of 'fresh' solid surfaces aiding the reaction rate enhancement. This result was confirmed by the similar rates of dehydrogenation seen at 200°C thermal and 160°C sonicated reaction conditions.

It seems that as the thermal reaction progressed the efficiency of the catalyst was reduced. It should be therefore possible to re-activate a thermal reaction by adding a second 'fresh' amount of catalyst. A thermal reaction was run for 5 hours upon which fresh catalyst was added this resulted in a slight jump in reaction rate which again began to 'tail off' requiring a further addition of catalyst (see Table. 6.2 and Fig. 6.2).

Fig 6.1 - Comparison of reaction conditions for the dehydrogenation of tetrahydronaphthalene



Thermal\Sonicated Tetrahydronaphthalene

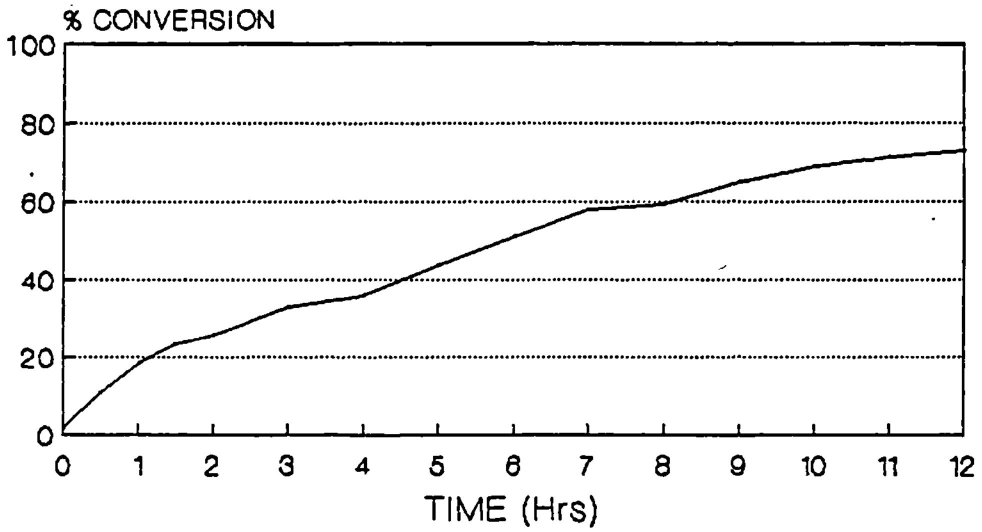
Table. 6.2 - % Conversion of tetrahydronaphthalene via thermal dehydrogenation at 200°C with 2 additions of fresh catalyst.

TIME (hrs)	% CONVERSION
0	1.7%
0.5	10.6%
1.0	18.2%
1.5	23.4%
2.0	25.6%
3.0	32.9%
4.0*	35.9%*
5.0	43.7%
6.0	51.0%
7.0	57.9%
8.0**	59.5%**
9.0	64.9%
10.0	69.0%
11.0	71.5%
12.0	72.9%

* Further addition of fresh catalyst
** Another addition of catalyst

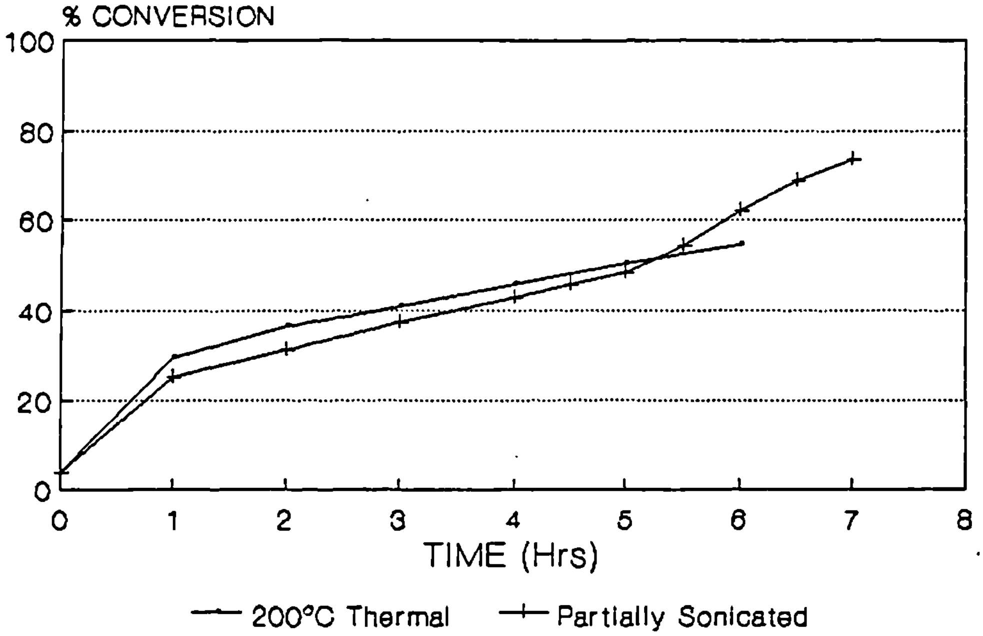
Even after 12 hours reaction time with 2 extra additions of catalyst the % conversion was still only 72.9%. It would seem some sonication was necessary in order to achieve reaction completion.

Fig 6.2 - Reactivation of a dehydrogenation reaction by the addition of fresh catalyst



'Reactivation' using 'fresh' catalyst

Fig 6.3 - Reactivation of a dehydrogenation reaction by the application of sonication



'Reactivation' employing sonication

If sonication results in catalyst activation it should be possible to 'rejuvenate' a thermal reaction which has run its course. An experiment was performed (see Table. 6.3 and Fig. 6.3) where a thermal reaction was stirred for 4.5 hours, when the reaction rate fell sonication was applied and the reaction was indeed 'activated'. The % conversion of tetrahydronaphthalene to naphthalene was pushed above that previously achieved under completely thermal conditions. Although the reaction was not followed to completion the advantages of sonication were clearly seen.

Table. 6.3 - Investigation into the re-activation of a thermally completed reaction by the application of sonication.

TIME (hrs)	% CONVERSION
0*	4.0%
1.0*	25.2%
2.0*	31.4%
3.0*	37.5%
4.0*	42.9%
4.5**	45.9%
5.0**	48.5%
5.5**	54.3%
6.0**	62.3%
6.5**	68.9%
7.0**	73.5%

* Thermal reaction conditions
** Sonicated reaction conditions

Assuming the rate of catalyst activation was dependant upon sonication an increase in power input should result in an increase in dehydrogenation rate. The results obtained from the dehydrogenation of tetrahydronaphthalene at 20% power output and 32% power output confirmed this (see Table. 6.4 and Fig. 6.4). Increasing the sonication power resulted in an increase of sonication intensity per each 1cm^3 of reaction volume. This increases the efficiency of catalyst surface cleaning and also increases mass transfer thus aiding dehydrogenation.

Table. 6.4 - % Conversion of tetrahydronaphthalene with respect to sonication power applied at 180°C.

TIME	20% POWER OUTPUT	32% POWER OUTPUT
1 hour	17.3%	17.6%
2 hours	19.1%	23.7%
3 hours	22.3%	27.2%
4 hours	24.0%	31.9%
5 hours	29.1%	36.8%
6 hours	31.8%	41.2%

The % conversions are low in this set of reactions due to the fact that the reaction volume was increased. As stated before an increase in volume results in a decrease in power intensity per every 1cm^3 of reaction volume.

If the dehydrogenation rate was indeed increased by catalyst surface cleaning and mass transfer, between catalyst surface and bulk solvent, then this could be verified using 'pulsed' ultrasound. A short high powered 'burst' of sonication should be enough to expose fresh catalyst active sites although the rate would then 'tail off'. We can use the pulse cycle of the sonicator to achieved such 'bursts'. The Sonics and Materials equipment has a pulse cycle lasting 1 second. When set at 50% pulse the sonication is

Fig 6.4 - The effect of alterations in applied power on the dehydrogenation of tetrahydronaphthalene

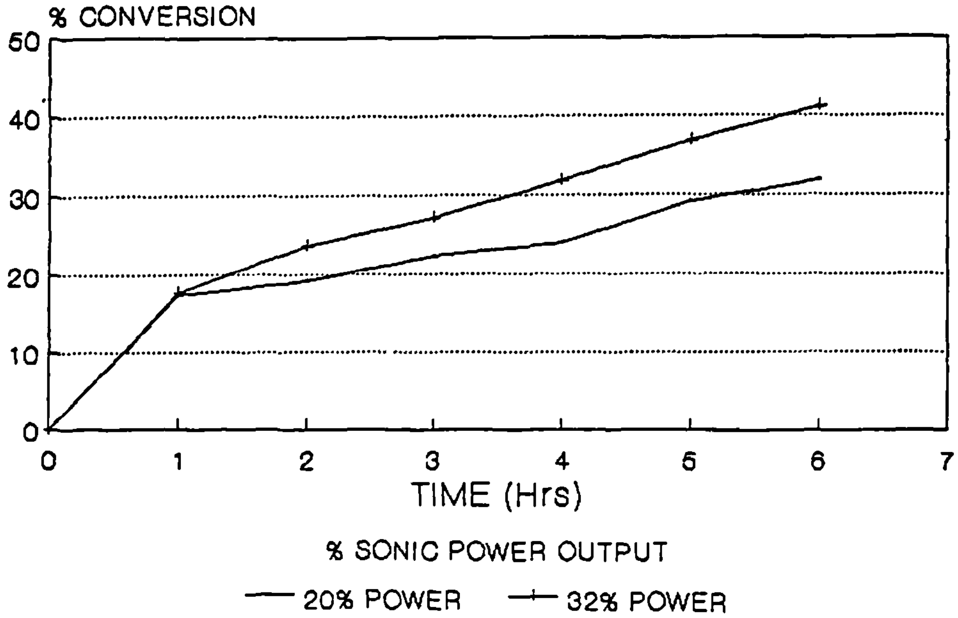
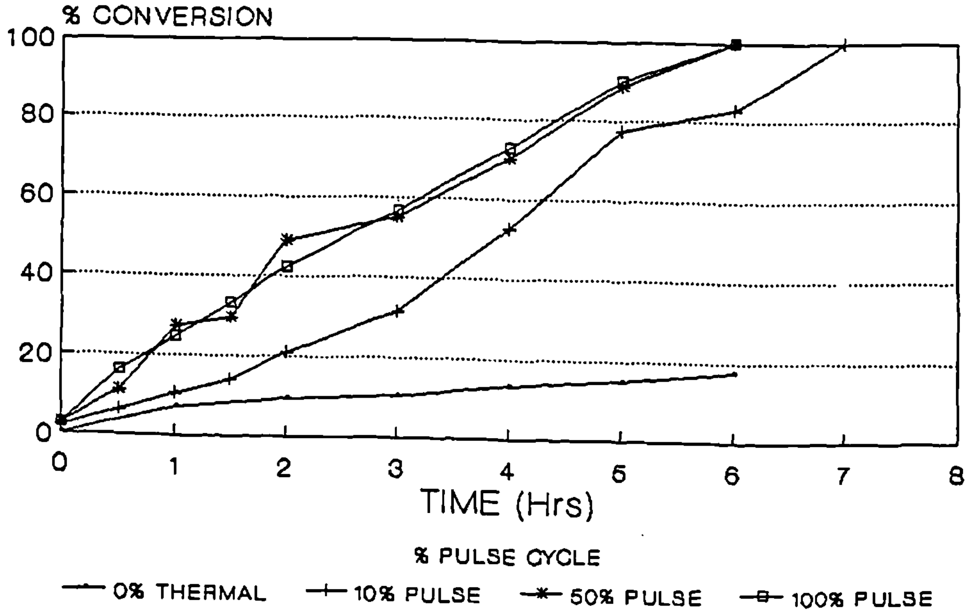


Fig 6.5 - The effect on the dehydrogenation of tetrahydronaphthalene by the introduction of a pulse cycle of sonication



applied for 0.5 second and then reapplied, for the same time period, at 0.5 second intervals. At 10% pulse sonication is applied for 0.1 seconds and then reapplied at 0.9 second intervals.

From the results obtained (see Table. 6.5 and Fig. 6.5) a 50% pulse cycle gave a similar rate of conversion to a fully sonicated reaction. However a 10% pulse cycle gave a slightly slower rate.

Table. 6.5 - % Conversion of tetrahydronaphthalene with respect to % Pulse cycle.

TIME	100% Pulse	50% Pulse	10% Pulse	0% (Therm)
0 hours	2.7%	2.5%	1.9%	-
0.5 hours	16.2%	11.0%	6.3%	-
1.0 hours	24.7%	27.3%	10.6%	7.1%
1.5 hours	33.1%	29.5%	14.0%	-
2.0 hours	42.5%	48.9%	21.1%	9.5%
3.0 hours	56.6%	55.0%	31.7%	10.6%
4.0 hours	72.7%	70.2%	52.7%	13.5%
5.0 hours	90.2%	88.9%	77.3%	15.2%
6.0 hours	100.0%	100.0%	83.1%	17.8%
7.0 hours	-	-	100.0%	-

All of the rates under sonication were much faster than the corresponding thermal reactions. These results indicated that continuous sonication was not necessary to achieve significant rate enhancement. Consequently considerable energy saving is possible.

The nature of the solvent used for sonicated reactions is very important (see earlier O-alkylation of 2,6-dimethylphenol). The dehydrogenation of tetrahydronaphthalene was attempted in a series of solvents and the thermal and sonicated reactions were compared (see Table. 6.6 and Fig. 6.6).

Fig 6.6 - The effect of solvent alterations on the dehydrogenation of tetrahydronaphthalene

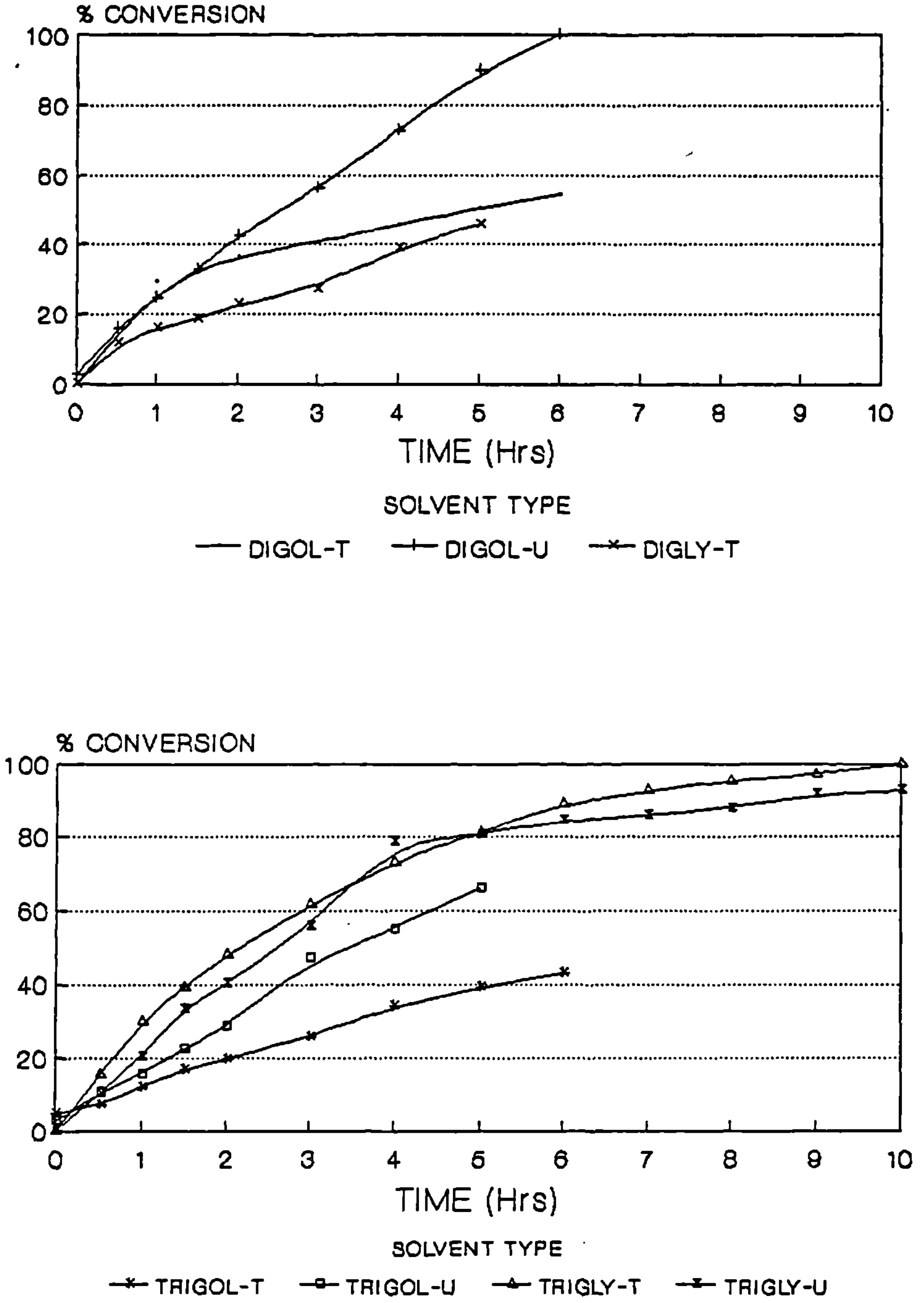


Table. 6.6 - % Conversion of tetrahydronaphthalene with respect to solvent type and mode of reaction.

REACTION SOLVENT EMPLOYED								
	DIGOL		TRIGOL		DIGLYME[a]		TRIGLYME	
TIME (hrs)	Th[b]	US[c]	Th	US	Th	US	Th	US
0	-	2.7	4.6	2.6	-	-	-	-
0.5	-	16.2	7.0	10.5	11.7	-	15.3	10.2
1.0	29.5	24.7	11.9	15.4	15.9	-	29.9	20.2
1.5	-	33.1	16.7	22.3	18.7	-	39.2	33.5
2.0	36.6	42.5	19.7	28.4	22.8	-	48.1	40.2
3.0	40.9	56.6	25.9	47.1	27.3	-	61.5	55.9
4.0	45.9	72.7	34.0	54.7	38.9	-	73.0	78.6
5.0	50.6	90.2	39.2	66.1	46.0	-	81.3	80.6
6.0	54.6	100.0	43.0				88.9	84.4
7.0							92.6	85.6
8.0							95.3	87.9
9.0							97.1	91.5*
10.0							100.0	92.7

* - Further addition of fresh catalyst, reaction completion not reached.

a - Sonication with diglyme was not attempted because the solvent boiling point at 162°C is too low for efficient cavitation and successful rate enhancement for this particular system. The thermal reaction was performed at approximately 160°C.

b - Thermal reactions all at 200°C.

c - Sonicated reactions all at 180°C.

The thermal reactions were attempted at 200°C and the most efficient reaction at this temperature was in triglyme (triethyleneglycol dimethyl ether). In this solvent after 5 hours reaction there was 81% conversion of the starting material to the expected product with the reaction complete after 10 hours. In diglyme (diethyleneglycol dimethyl ether) 46% conversion was reached, at the maximum attainable (but lower temperature) of approximately 162°C (the solvent boiling point). Thermal reactions in digol (diethyleneglycol) and trigol (triethyleneglycol) gave poor results with approximately 50% and 40% conversion, respectively, after 5 hours at 200°C. It therefore appears that the 'ether' type solvents, triglyme and diglyme, produce a more efficient thermal reaction. The influence of the hydroxyl group on the solvent structure would thus appear to be a disadvantage under thermal conditions.

Application of sonication to the dehydrogenation of tetrahydronaphthalene in triglyme at 180°C resulted in no rate enhancement over the corresponding thermal reaction. However sonication of the reaction in either digol or trigol resulted in significant rate enhancement, approximately 80% and 70% enhancement respectively, when compared to the corresponding thermal reaction at the higher temperature of 200°C.

The sonicated reaction in digol reached completion after only 6 hours reaction time, whereas 10 hours were required to complete the thermal reaction in triglyme.

The importance of the boiling points (and vapour pressures) of the solvents employed in sonicated reactions has been referred to earlier. The table below confirms that digol and trigol should produce the most effective cavitation and thereby generate the greatest sonochemical enhancement.

Boiling points as follows:-

Triethyleneglycol (trigol) - 285°C

Diethyleneglycol (digol) - 245°C

Triethyleneglycol dimethyl ether (triglyme) - 216°C

Diethyleneglycol dimethyl ether (diglyme) - 162°C

6.5 CONCLUSION

In summary it would appear that high boiling ethereal solvents, such as triglyme and diglyme, are the most efficient solvents for thermal dehydrogenation. The preferred solvents for a sonicated reaction are the higher boiling hydroxy solvents, such as trigol and digol.

Dehydrogenation may certainly be enhanced by the application of sonication. Efficient dehydrogenation was shown to occur at 20-40°C below the corresponding thermal reaction temperature. Constant sonication was not necessary as use of a 50% pulsed cycle achieved a similar rate of reaction. Reaction completion was also achieved without further additions of 'expensive' catalyst.

Sonication may aid previous 'reluctant' dehydrogenations and also introduce the use of lower boiling, less expensive solvents, always an interest in industrial applications.

CHAPTER 7

EFFECT OF ULTRASOUND ON SOLIDS AND DISPERSIONS

7.0 EFFECT OF ULTRASOUND ON SOLIDS AND DISPERSIONS

7.1 INTRODUCTION

It is the use of power ultrasound within the food industry which has recently generated considerable interest. High frequency low power ultrasound has been employed within the food industry for many years as a non-invasive diagnostic method of analysis, for the measurement of factors such as the efficiency of emulsification within dispersions and the concentration and/or degree of dispersion of particulate matter within a liquid.

Low frequency high power ultrasound is known to enhance and/or alter the characteristics of many chemical reactions. In this study we have investigated the potential for the use of high power ultrasound in processing to alter the characteristics of various types of foodstuff.

High Frequency Ultrasound

High frequency low power ultrasound, with frequencies between 0.5 - 20MHz, may be employed to evaluate and characterise foodstuffs with regard to their physical characteristics such as described above. This is achieved by measurement of the sound velocity and/or sound attenuation of a short pulse of ultrasound, when passed through a food sample. Thus by monitoring the attenuation of a pulse of ultrasound when it was passed through a sample of milk or cream Miles et al[84] determined the degree of homogenisation of fat within the sample. By comparing whole milk to skimmed milk the degree of attenuation due to the fat content of the milk could be determined.

Sound attenuation in milk and cream is mainly due to heat transfer in and out of fat globules. As the degree of fat homogenisation increases *i.e.* as fat droplet size decreases sound attenuation also increases. Thermal losses account for most of the sound attenuation observed. Losses due to viscosity factors and signal scattering account for a minimal amount of sound attenuation in this type of system.

The velocity of sound has been employed to determine the degree of emulsification or concentration of a sample. The 'time of flight' of a sound signal through the sample can be monitored via a transmitter and receiver system which need not be in direct contact with the liquid. This method was employed to determine the degree of emulsification in samples such as salad cream. and can also be employed in conjunction with attenuation measurements to determine factors such as the degree of 'creaming' of a sample, the movement of solid particles/fat droplets to the surface, and fat droplet sizes within the sample. Such information gives details, for example, of the long term stability of fruit juices, the age of eggs and the stability of emulsions such as mayonnaise.

This method of analysis is non-invasive and therefore non-destructive and non-hazardous. It may be connected to 'on-line' production processes thus allowing automation. It is also economic as equipment often involves a single transducer acting as transmitter and receiver employing pulse/echo techniques.

Low Frequency Ultrasound

Low frequency high power ultrasound, with frequencies between 20kHz - 1MHz, can be employed directly to alter the characteristics of food.

It has been shown that sonication of aqueous solutions results in the production of hydrogen and hydroxyl radicals. The presence of radicals within food samples may aid oxidation/reduction processes which may either be advantageous or detrimental to the characteristic properties of the food.

Increased rates of oxidation in products such as wines and spirits are desirable for flavour development and early maturation of the product. Sonication has been successfully employed to enhance the flavour of wines and spirits. However in fats the converse applies. Gordon[85] states that the most common path to flavour deterioration in fats is the auto-oxidation of triacylglycerols. Auto-oxidation is a free radical reaction in which the main initiators are hydroperoxides which decompose above 150°C, although decomposition does occur slowly below this temperature. Decomposition results in the formation of various volatile products which cause changes in the flavour of the fat. Enhanced rates of oxidation via sonication would therefore not be desirable in such products and must be carefully monitored.

Ultrasound has been known to affect the emulsification of food. Sonication provides a more stable emulsion without it being necessary to add surfactant. Emulsions with smaller droplet sizes within a narrow size distribution are obtained, when compared to other methods of emulsification. Industrially products such as salad cream, tomato ketchup, peanut butter and some cream soups are produced in this manner.

Extraction of products can also be enhanced by employing ultrasound. Chendke and Fogler[86] examined the rate of ultrasonic extraction of sugar from sugar beets. They discovered that the disruption of cells via cavitation effects results in the subsequent release of cell contents into the bulk medium. This combined with enhanced mass transfer, due to the effects of microstreaming, all result in a more efficient method for sugar extraction.

Zhao et al[87] studied the sonicated extraction of medicinal compounds such as helicid, berberine hydrochloride and bergenin from Chinese plants. In some cases sonication increased the efficiency of extraction at lower temperatures producing a purer product in a shorter time. Helicid is normally extracted by refluxing in ethanol but sonication produced 50% more product in half the extraction time at room temperature. Once again efficient cell disruption and effective mass transfer is attributed to these results.

Sonically enhanced crystallisation has been observed in many systems, for example the crystallisation of water in the presence of sonication produces more uniform ice crystals at a faster rate. Sonically induced crystallisation of sucrose solutions has also been investigated, see later. To be able to control the point at which crystallisation occurs would be a great advantage in any large scale production process. Often crystallisation can occur in an uncontrolled manner simply due to a slight drop in temperature or pressure. On the other hand to control the initiation of crystallisation is often difficult since problems may occur due to incorrect external factors such as temperature and pressure settings. Sonication is thought to enhance both the nucleation rate and rate of crystal growth in a saturated or supercooled medium by producing fresh and/or more nucleation sites in the medium. This may be due to cavitation bubbles acting as nuclei for crystal growth or by the disruption of seeds/nuclei already present within the medium thus increasing the number of nuclei present in the solution/melt.

The ability to defoam liquids by the use of ultrasound is becoming useful in many types of industrial operations. Although the mechanism of defoaming is not fully understood it is assumed that the combination of negative pressure at the bubble surface due to cavitational collapse and the following wave of high pressure, with bubble coalescence also occurring, all result in effective defoaming.

In industry ultrasonic defoaming is currently used during the bottling and canning process of various carbonated liquids. It is also employed in sewage treatment plants for the defoaming of waste products.

Removing unwanted air or gases is a requirement for many food processes and it can be extremely difficult especially in very viscous liquids such as chocolate. Ultrasound has been employed to degas liquids as viscous as molten glass and as dense as molten metals during their solidification process and also less viscous liquids as in the defoaming of beer and carbonated drinks[88].

Ultrasonic filtration of particulate matter from a liquid is now arousing some interest. The rate of slurry flow through a filter can be increased substantially if ultrasound is applied in the vicinity of the filter.

Fairbanks and Chen[89] obtained an 18 times increase in filtration rate of motor oil through a sandstone filter when insonating the sample 15cm above the filter. Semmelink[90] examined the effect ultrasound has on tap water flow through a metal wire cloth resulting in a rate increase of up to 300 fold in the presence of ultrasound. In some cases ultrasonic irradiation prevents the formation of a filter cake on the filter. It appears that cavitation and microstreaming lead to a cleaning effect on the surface of the filter and increases the flow through the filter pores.

The use of ultrasound has enabled the development of a new efficient method of filtering particulate matter from a flowing material a patent application describes the novel process[91]. Previous methods of filtration involved placing filters in the flow pathway, which restricted flow and required regular maintenance, or diverting the flow in such a manner that the particulate matter is filtered off via centrifugal effects. Now a simple non-invasive method of filtering a flowing liquid has been developed which involves setting up standing waves in a column of liquid. If a sound beam is transmitted and then reflected back interference of the wave pattern occurs. Positive interference results in the formation of a node of high intensity sound and negative interference results in antinodes.

On formation of the standing wave any particulate matter in the flow will gather at the nodal points. By varying the frequency of the sound beam slightly a drift on the standing waves may be produced and the particles move with the waves to a possible collection point. It is also possible to separate different sizes of particles as those strongly attached to the standing wave will move with it and others will drop and be picked up by the following wave. Standing waves may also be produced by two transducers opposing each other producing interfering beams of sound. By varying the phase difference between the signals a drifting wave may be established.

Enhanced drying by the application of ultrasound has also aroused interest. Fairbanks[92] investigated the drying of coal particles in the presence and absence of ultrasound. By passing warm air of 65°C over the drying surface of the coal and applying ultrasound directly to the surface of the coal particles it was possible to substantially increase the rate of drying and also reduce the moisture content of the final dried sample. This is thought to be initially due to a reduction of pressure above the sample to encourage water loss. Intensity of sonication and particle size of the coal proved to be limiting factors. The size of the particles greatly affect the characteristics of the liquid filled channels present within the sample and may reduce the capillary action necessary for efficient drying.

The use of ultrasound in processing creates novel and interesting avenues to be explored. Ultrasound provides an effective method for the non-invasive analysis of an on-line production process. It also provides a route to enhanced rates of extraction , filtration and drying which all combine to reduce processing times and increase efficiency. There is a wide scope for the future use of ultrasound within processing and manufacture which should be explored further.

7.2 EFFECT OF ULTRASOUND ON RICE GRAINS

7.2.1 INTRODUCTION

In today's 'market place' white rice can be found in many forms. It is frequently seen in 'labour saving' packages in which it is partially cooked before being packaged. Completion of the cooking process may be easily achieved by the customer later on by the addition of boiling water in food products such as 'Pot Rice'. At this present time no such alternative exists for brown rice. Brown rice still retains its hard outer shell/kernel and thus cooking times are prolonged as the absorbtion of water into the rice grain, and subsequent swelling of the grain, is inhibited until cooking is completed. Nevertheless there is a perceived customer requirement for more 'wholesome' food like brown rice.

In these health conscious days promotion of brown rice by the development of a wider range of novel products would be welcomed. It was thought that the effects of ultrasound on solid surfaces, well known in heterogeneous chemical reactions, may be used to advantage in the disruption of the brown rice shell thus allowing for a much reduced cooking time.

The reduction of solid particle size by ultrasound has resulted in many experimental studies and the phenomenon is now quite well characterised. It is thought that under the influence of sonication cavitation bubbles are formed within the solvent. When these bubbles are formed near a solid surface, asymmetric growth occurs. On cavitational collapse an uneven collapse of the bubble results in a microjet of liquid being propelled forwards at great speed towards the solid surface, high speed photography has provided evidence for this phenomenon. This microjet is thought to cause pitting and erosion of a bulk solid surface, such as that observed in large blocks of catalysts and is thought to be the basis for surface cleaning and enhanced mass transfer to the solid surface. (See earlier Chapter 4 for particle size reduction and microjet phenomena).

Sonication of a solid suspension of rice in water would be expected to produce surface erosion and particle size reduction due to the large size of the rice grains inducing bubble deformation and microjet formation and also due to the brittle nature of the solid.

7.2.2 EXPERIMENTAL CONDITIONS

7.2.2.1 Thermal Reaction Conditions

The standard reaction conditions were employed as quoted in section 2.5.1.

7.2.2.2 Sonicated Reaction Conditions

Reaction conditions employing the sonic probe system as quoted in section 2.5.2.1.

Reaction conditions employing the sonic bath system as quoted in section 2.5.2.2.

Reaction conditions employing the tube reactor system as quoted in section 2.5.2.3.

7.2.2.3 Sonication of a 50/50 mixture of Brown and White Rice

The standard reaction conditions were employed as quoted in section 2.5.2.1 but the rice sample contained 25g of brown and 25g of white rice.

7.2.2.4 THE EFFECT OF ULTRASOUND ON STARCH EXTRACTION

Reaction conditions as for section 2.5.3.

7.2.2.5 MICROWAVE CONDITIONS

Standard reaction conditions as for section 2.5.4.

7.2.2.6 THE EFFECT OF SONICATION ON THE GELATION OF GROUND RICE

Thermal reaction conditions

As for section 2.5.5.1. However 25g of ground rice was employed. The rice mixture began to thicken as 68.0°C was reached. After 6.5 minutes 70°C was attained and maximum density was achieved. A very granular gel was obtained.

Sonicated reaction conditions

Sonic probe

As for section 2.5.5.2. However ground rice was employed. The solution thickened after 9 minutes as 67°C was reached and sonication was no longer possible after 10 minutes 20 seconds. A dense lumpy mixture was obtained which was less granular than the gel obtained thermally. This suggested that the size of the rice granules must have been reduced on sonication.

The rice mixture was then treated as for section 2.****. A lumpy gel with a smaller grain size was obtained after 6.5 minutes as 70°C was attained.

Sonication does not reduce the time or the temperature of ground rice gelation. It does however appear to reduce the grain size.

7.2.3 RESULTS/DISCUSSION

Thermal gelation of white rice was attempted at several temperatures and it was discovered that gelation did not occur below the temperature range of 75 - 80°C. The relatively high temperatures are thought to be necessary in order for water to efficiently penetrate the rice shell. At 80°C white rice gelled within 15 minutes and brown rice within 25 minutes.

Rice grains are composed of a hard outer shell with a centre containing mainly rice starch. On the addition of water and heat, necessary for thermal gelation, the rice grains swell as they begin to absorb and retain water within their starchy centres. As the rice grains expand starch may become released into the surrounding medium due to the splitting of the rice shell - noticeable as the cloudy water which is obtained when rice is boiled. In white rice the hard outer shell of rice grains has been removed to give its lighter colouration, unlike brown rice which still retains it shell. The white rice grains are therefore more exposed to the surrounding medium as their external protection layer has been removed. This results in a faster thermal gelation.

Rice grains were initially sonicated, with a sonic probe, below 75°C to determine if gelation can occur at lower temperatures. No significant gelation was observed with sonication at these temperatures and it was concluded that the gelation and swelling of the starch, is probably a thermal effect.

Probe sonication was not attempted above 75°C, *i.e.* approaching the boiling point of the water/rice mixture (approximately 95°C). It was considered that sonication attempted at these temperatures would lead to cavitation bubbles filled with water vapour so that cavitational collapse would be 'cushioned' and thus less effective.

In order to use the energy of cavitation an approach was used whereby the rice was 'pre-sonicated' at a lower temperature. In this way the maximum surface attack/ particle size reduction could be generated before the sample was raised to the normal gelation temperature. The rice grains were sonicated with the Sonics and Materials equipment employing a sonic probe with a 1.2cm tip at room temperature for a period of 1, 5 and 10 minutes at power settings of 2,4,6 and 8. The pre-sonicated rice was then placed in a water bath and the temperature raised to 80°C and the time taken for gelation to occur at this temperature was noted.

The results for both white and brown rice clearly demonstrated, see Table. 7.1 and Fig. 7.1, that the longer the pre-sonication time the shorter the time of gelation. For brown rice an increase in the power applied reduced the time of gelation. For white rice however an increase in power applied did not produce significant differences in the time of gelation and low power settings were sufficient to enhance gelation time considerably. These results indicated that power ultrasound is potentially very useful as a pre-treatment for brown rice in that it appears to reduce the 'protection' afforded by the hard shell of the grain.

Table. 7.1 - Comparison of gelation times of white and brown rice under thermal and sonicated reaction conditions once 80°C has been attained.

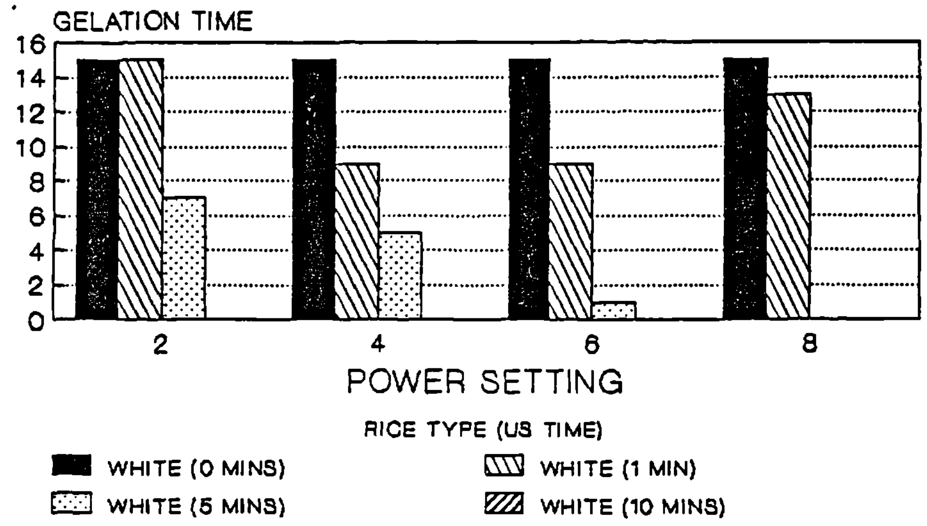
	WHITE RICE				BROWN RICE			
POWER APPLIED	2	4	6	8	2	4	6	8
Sonication Time	**Gelation Times at 80°C**							
0 mins*	15	15	15	15	25	25	25	25
1 mins	15	9	9	13	25	22	17	20
5 mins	7	5	1	0	20	17	15	15
10 mins	0	0**	0	0	22	12	10	5

* - Thermal reaction conditions.

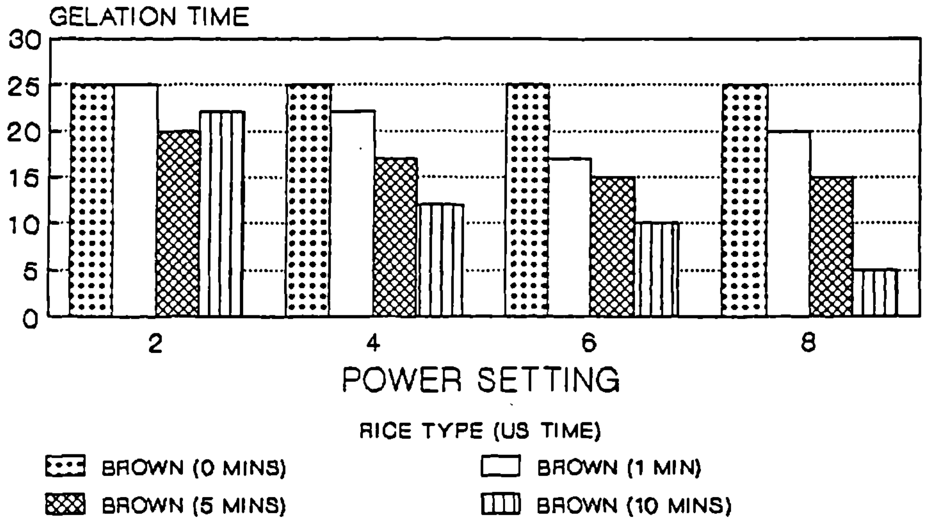
** - 80°C not reached before gelation is completed due to very efficient starch release.

Fig 7.1 - Comparison of gelation times of rice under themal and sonicated reaction conditions

WHITE RICE



BROWN RICE



In order to verify the disrupting effect on the surface of rice grains produced by pre-sonication a series of photographs were obtained.

Initial photographs before sonication clearly show the hard shell present in brown rice and its total absence in white rice, see figs 7.2 and 7.3. After 1 minute sonication brown rice exhibits no erosion of its outer shell, fig 7.4, whilst white rice begins to indicate some particle size reduction of the grains, fig 7.5. After 5 minutes sonication brown rice exhibits very slight surface erosion, see fig 7.6, whilst in complete contrast the white rice grains show a large extent of grain destruction. Grain particle sizes are much reduced with the centre of the rice grains, containing starch, clearly exposed, see fig 7.7. Further sonication of the grains, 10 minutes, now begins to indicate particle size reduction and grain destruction in the brown rice grains with some exposure of their starch centres, see fig 7.8. Whilst white rice grains now bear no similarity to their original grains with sizes much reduced and starch centres exposed and in some cases absent, see fig 7.9, indicating release of starch into the surrounding medium.

The photographs indicate that sonication is very effective in erosion of white rice grains. The fast particle size reduction and release of starch to the surrounding medium results in a much increased gelation time with a 'finer' gel obtained. In contrast the hard shell of the brown rice hinders the early release of starch and it is only when the surface becomes disrupted enough to expose the internal grain contents that gelation time is significantly reduced. Gelation time can thus be related to the efficiency of starch release to the surrounding medium.

Pre-sonication of white rice grains with a small sonic bath produced no improvement over conventional thermal methods. The intensity of the sonication was not sufficient to disrupt rice the surface of the rice and expose the internal starch.

INITIAL APPEARANCE - 0 MINS SONICATION

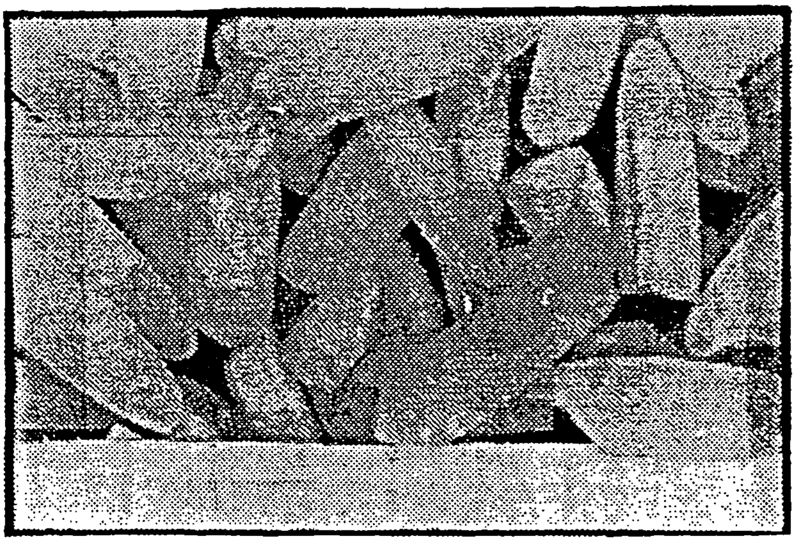
Fig 7.2 BROWN RICE

Fig 7.3 WHITE RICE

1 MIN SONICATION

Fig 7.4 BROWN RICE

Fig 7.5 WHITE RICE



5 MINS SONICATION

Fig 7.6 BROWN RICE

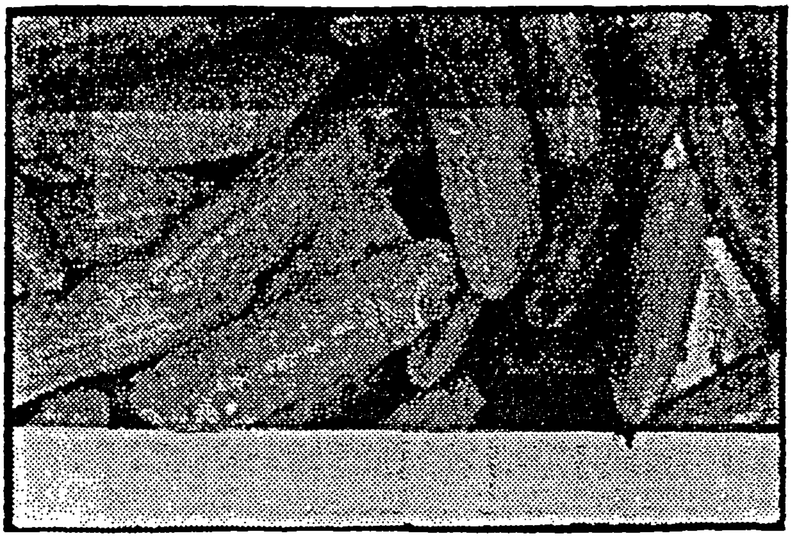
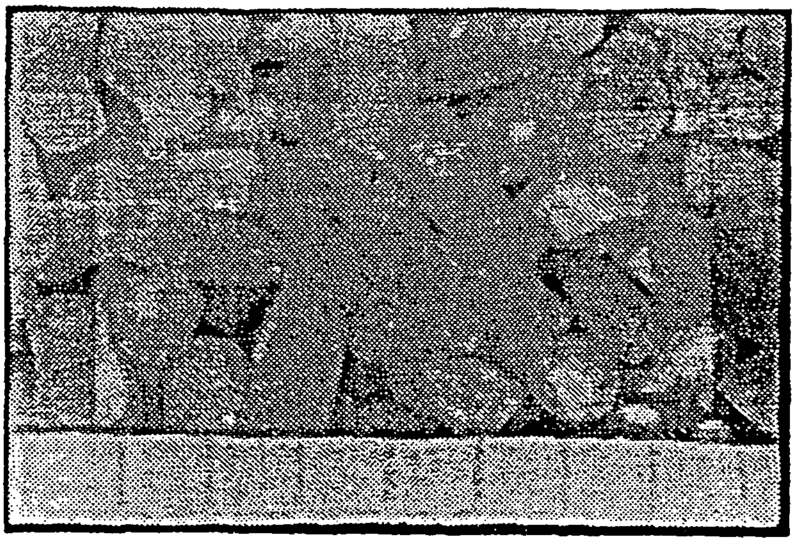


Fig 7.7 WHITE RICE



10 MINS SONICATION

Fig 7.8 BROWN RICE

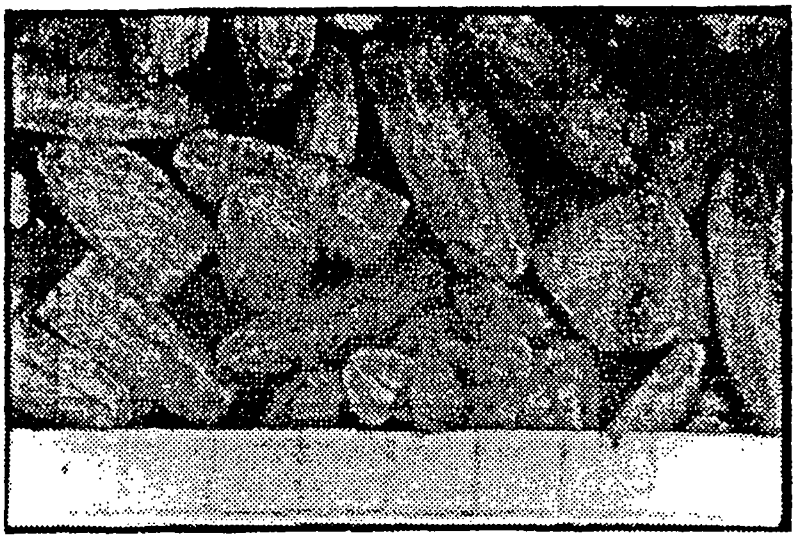
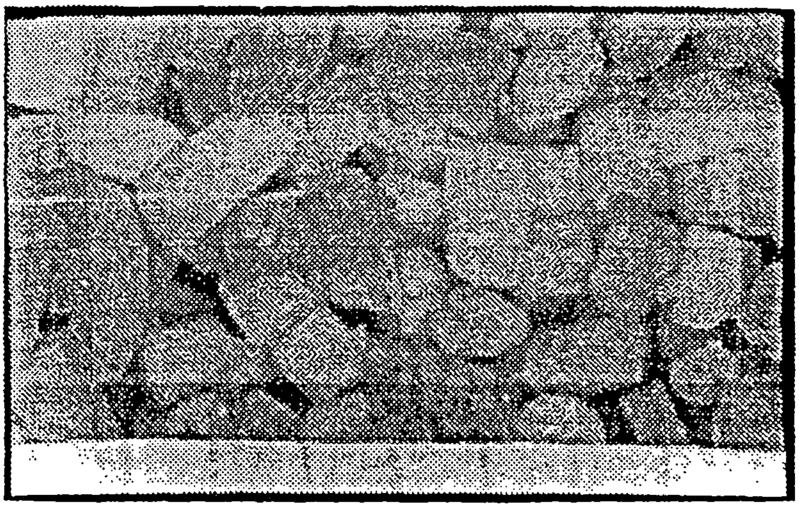


Fig 7.9 WHITE RICE



Sonication of a mixture of white rice employing the sonic bath produced no improvement over conventional thermal methods. Pre-sonication of the rice at 25°C and sonication at 80°C produced no improvement over conventional thermal methods. Sonication of brown rice however produced some improvement and it appears that sonication is beginning to reduce the barrier to rice gelation provided by the rice shell.

Sonication using the pentagonal tube reactor, see earlier, proved to be somewhat difficult. Initial problems were encountered in attempting to disperse the rice grains evenly throughout the medium (*i.e.* throughout the ultrasonic field). The tube reactor is a vertical tube of approximately 32cm length and 7cm diameter. On addition of a water/rice mixture to the tube the heavy rice grains settle to the base of the tube. Due to the small tube diameter mechanical stirring was not sufficient to produce a vortex powerful enough to raise the grains from the base and keep them dispersed. Due to the inefficient dispersion of rice grains into the 'sonication field' of the reactor a less efficient particle size reduction and/or surface disruption was observed resulting in no improvement over corresponding non-sonicated thermal results.

As stated previously sonication of white rice results in sufficient levels of starch release to reduce the time of gelation, whilst in brown rice the levels of starch released are much lower. In an experiment a 1:1 ratio of brown to white rice was sonicated and the time taken for the rice to gel was noted. For an equivalent sample of 100% white rice the time taken to gel was 0 minutes, *i.e.* reaching 80°C was not necessary as sufficient starch was released into the bulk medium to allow gelation to occur. The equivalent experiment with 100% brown rice resulted in gelation occurring after 15 minutes at 80°C. For the 1:1 rice mixture gelation was attained after 8 minutes, *i.e.* in half the time.

Sonication of the white rice releases enough starch to ensure gelation of the whole rice mixture.

STARCH RELEASE FROM RICE GRAINS

Starch is a valuable commodity in the food industry, see later, and it is used extensively in many industrial processes. Sonication of rice appears to release starch into the surrounding medium and so an examination of the starch levels released on sonication of white and brown rice was attempted.

White and brown rice grains were washed and dried in an oven at approximately 65°C. 50g of rice was added to 100cm^3 of distilled water and the mixture was either sonicated or stirred vigorously for 5 minutes. The supernatant water was filtered through two porosity No3 filters to retain any starch released into the surrounding medium. The remaining rice shells were washed with a further 500cm^3 of water, which was carefully filtered to recapture any starch. The rice remains/ shells were then oven dried at 65°C as was the collected starch. The amount of starch recovered was calculated, see Table 7.2.

From the results obtained it can be observed that sonication provides an efficient method for starch extraction from rice grains. In white rice grains release of starch into the bulk medium in the presence of sonication is 16 times more efficient than in its absence. For brown rice the efficiency is up to approximately 30 times more efficient in the presence of sonication.

Table. 7.2. The efficiency of starch extraction from white and brown rice grains.

	White Sonicated	**White Stirred**	**Brown Sonicated**	**Brown Stirred**
Mass Of Rice	50.00g	50.00g	50.00g	50.00g
Mass Of Beaker	100.48g	96.25g	97.85g	94.10g
Mass Of Beaker Plus Rice Remains	122.28g	144.5g	142.69g	142.65g
Mass Of Rice Remains Recovered	**21.8g**	**48.25g**	**44.84g**	**48.55g**
Mass Of Petri Dish	35.31g	26.68g	35.11g	14.80g
Mass Of Starch Plus Petri Dish	63.59g	28.41g	38.08g	14.89g
Mass Of Starch Recovered	**28.28g**	**1.73g**	**2.97g**	**0.09g**

When comparing white rice grains to brown rice grains it was observed that the presence of a rice shell reduced the efficiency of grain size reduction and grain disruption. The protective surface barrier has first to be broken open before the starch contents can be released. In the presence of sonication the extraction of starch from white rice is approximately 10 times more efficient than that observed with brown rice.

GELATION OF RICE EMPLOYING MICROWAVES

Another method of rice preparation is the use of microwaves to heat and 'cook' rice. The gelation of white rice was attempted using microwaves in a domestic oven in order to compare with results obtained via ultrasonic and thermal treatment of rice.

Microwave irradiation raises the temperature levels of water very effectively with little effect on the rice grain temperature. This results in a tendency to vapourise the water when using conventional rice/water mixtures. To compensate for this the water content in the rice/water mixture was doubled. Gelation was not attained on microwave irradiation. Starch was not released into the surrounding medium in large amounts as the rice grain size was not effectively reduced and the grain shell was not disrupted resulting in poor gelation. It would appear that the use of microwaves has limited use in rice gelation.

GELATION OF GROUND RICE

It appears that more effective gelation of starch is associated with a more efficient release of starch into the surrounding medium. We have shown that ultrasound enhances this release by initially disrupting the rice shell and then reducing the rice particle size for both white and brown rice.

Ground rice has the smallest commercially available rice grain size. The rice grains have been mechanically ground to very small particle sizes resulting in total disruption of the rice shell and release of starch contents. An experiment was performed in order to observe how ground rice compared with the results obtained via thermal and ultrasonic treatment of rice. A more effective rate of gelation would be expected with ground rice for the reasons given and this is observed with a thermal gelation time of 6.5 minutes at 70°C compared with 15 minutes at 80°C with unprocessed rice, a 56% more efficient gelation at a much lower temperature.

Problems exist in the sonication of ground rice due to the extreme viscosity of the solution as gelation begins. After 1 minute 20 seconds at 67°C sonication is no longer possible as the solution is so viscous that levels of sound attenuation are great and cavitation cannot occur under these conditions. This results ultimately in an uneven distribution of sound and therefore uneven mixing of the solution and a 'lumpy' gel.

7.2.4 CONCLUSION

Pre-sonication of rice grains with a sonic probe appears to reduce gelation time considerably. In the case of brown rice the rice shell is initially attacked and disrupted and then rice particle size reduction occurs. In white rice particle size reduction begins at an earlier stage due to the absence of a protective shell. This all results in a release of starch into the surrounding medium resulting in a more effective gelation of rice at a lower temperature.

Ground rice, with most of its starch contents exposed, gelled at 10°C below the corresponding thermally treated rice with a 56% increase in rate of gelation.

Sonication employing a sonic bath provided little improvement over conventional thermal methods due to the low levels of power involved, providing little particle size reduction or surface disruption. Problems were encountered using the pentagonal tube reactor because it proved to be impossible to maintain the rice particles suspended in the ultrasonic field. This system therefore showed little enhancement over conventional thermal methods. Microwave irradiation provided very limited gelation of rice due to the lack of starch release into the bulk medium.

In conclusion pre-sonication of rice, employing sonic probe, is an effective method of increasing the rate of rice gelation and reducing the temperature at which this occurs. Rice grain size is also effectively reduced. Release of starch is very effective in a short space of time and this may also be a method of obtaining starch for use in other areas of the food industry, see later.

7.3 EFFECT OF ULTRASOUND ON THE SIZE DISTRIBUTION OF SUGAR

7.3.1 INTRODUCTION

It has been shown that the application of sonication to a solids dispersion results in disruption of the solid surface, see above, and also a reduction in solid particle size.

An investigation into the effects of sonication on a dispersion of sugar in vegetable oil was examined. This was not viewed as a method of producing caster sugar from the larger grained cane sugar, because this is readily and effectively achieved via controlled crystallisation of the crude sugar syrup. It was viewed more as a method of avoiding the expense of employing a more refined, smaller grained sugar for the processing and production of small grain size products, such as fudges and fondants, by employing crude sugar and achieving the required grain sizes by the sonication of the crude sugar mixture.

It may also be possible to produce a more desirable product as sonication of the crude sugar dispersion could reduce the dispersity of the sugar grain sizes and produce more uniform sugar crystals resulting in a 'smoother' less granular texture in the product.

7.3.2 EXPERIMENTAL CONDITIONS

Sonic Probe

The standard reaction conditions were employed as for section 2.6.1.

Tube Reactor

The standard reaction conditions were employed as for section 2.6.2.

7.3.3 RESULTS/ DISCUSSION

Selection of the sugar size to be studied in the following particle size experiments presented a problem. The average size of granulated cane sugar, determined by scanning electron microscopy, was 1000μm in diameter. The Galai particle sizing equipment employed measures to a maximum of only 150μm diameter. Although the sugar granules can be observed with the naked eye and particle size reduction is clearly observed it was not possible to determine the extent of size reduction until the size was reduced sufficiently to register on the Galai equipment. However the time taken for the granulated sugar size to become so reduced that it could be measured was noted and the average grain size at this point was determined.

Caster sugar, although being finer and of smaller grain size than granulated sugar, has an average size of 500μm, still too large for effective use with the particle size equipment. On the other hand icing sugar, with an average grain size of approximately 55μm, is well within the Galai particle sizer limits. Sugar size for this system can thus be determined from the onset of sonication to completion of the experiment.

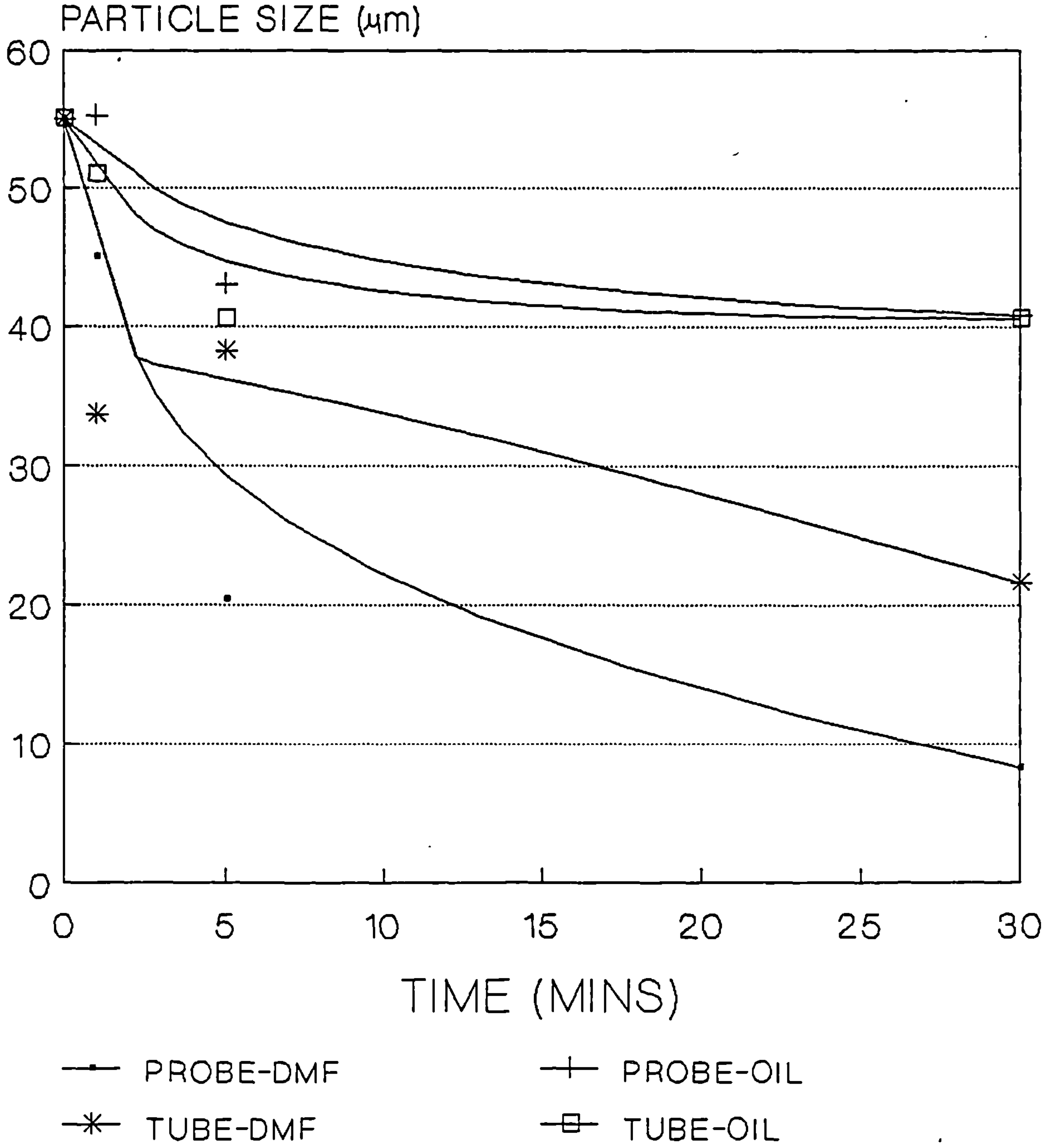
It was originally hoped that particle size reduction could be attempted in vegetable oil, a good medium in the food processing industry. However several problems were encountered. Vegetable oil is a viscous medium and sound attenuation is large. Due to the low specific heat capacity of the oil it heats up very quickly as sound energy is converted to thermal energy. This was not therefore a suitable medium for sonication. A second and unforeseen problem was discovered when attempting to measure the particle size of icing sugar in vegetable oil. Under normal conditions the solvent medium is placed within a cuvette with a magnetic stirrer. On addition of solid particles the stirrer is activated and the particles are driven upward into the detection beam by the vortex formed within the solvent medium by the stirring action. Vegetable oil proved to be too viscous for efficient vortex formation and the sugar particles remained at the base of the cuvette and were thus undetected. It was necessary to find a less viscous solvent, which did not dissolve sugar, in order to be able to measure any changes in sugar particle size.

The solvent chosen was dimethylformamide. It has a sufficiently low viscosity to enable use with the Galai particle sizing machine and will also propagate sound waves effectively. It has a high boiling point of 153°C, which results in a low vapour pressure, an advantage in producing effective cavitational collapse. Any cavitational effects were expected to be enhanced in this medium.

Sugar size reduction was attempted initially with a powerful 20kHz probe immersed directly into the sugar/ dimethylformamide mixture in an attempt to determine if size reduction is indeed possible. This proved to be an effective method of reducing sugar size for both granulated sugar and icing sugar. When oil was used as the medium however only granulated sugar was reduced in size and icing sugar seemed unaffected. This would suggest that there is a limiting particle size for effective reduction under these conditions, see Tables 7.3 and 7.4 and Fig. 7.10.

Several problems were encountered when the <u>tube reactor</u> was used for particle size reduction. Temperature control is limited and the reaction mixture temperature inevitably rises on sonication, in vegetable oil up to 120°C was reached after 60 minutes sonication. Addition of ice or the circulation of cold water through the tube reactor will disturb the standing waves and reduce the efficiency of sonication. The large volumes and masses involved with the tube reactor combined with the low specific heat capacity of the oil employed resulted in ineffective sonication of the reaction mixture. By employing a smaller diameter glass vessel, to contain the sugar and solvent mixture, and placing it in

Fig 7.10 - Average icing sugar grain size with respect to time, solvent and sonication method



SONICATED BY TUBE REACTOR OR SONIC PROBE water, which has a higher heat capacity than oil, cavitation may be more effective. The 26.5mm glass vessel, which provided us with the most effective sonication results when observing the sonication of potassium iodide, was employed (see earlier Chapter 3).

A second problem was the dispersion of sugar within the tube reactor, or reaction vessel, due to the large amounts involved. Icing sugar was fine enough to remain afloat within the solvent and this presented no difficulty in exposure to the sonic waves emanating from the tube walls. Granulated sugar however sank directly to the base of the tube reactor, or vessel, due to its weight. Attempts to stir this mixture presented its own difficulties. The mass of sugar sinking to the base of the tube impeded effective stirring, via an overhead mechanical stirrer, and the diameter of the tube also prevented the formation of an effective vortex necessary to lift the sugar off the bottom. These factors all combined to result in no crystal size reduction by the tube reactor for granulated sugar simply because the sugar was never exposed to the sonication zone.

Table. 7.3 - Average sugar grain size (μm) with respect to time, solvent and mode of sonication.

DIMETHYLFORMAMIDE				
	Icing Sugar		**Granulated Sugar**	
TIME	Probe	Tube	Probe	Tube
0 mins	55.0 ± 2.8	55.0 ± 2.8	1000 ± 50	1000±50
1 min	43.0 ± 2.2	33.7 ± 1.7	-	-
5 mins	20.4 ± 1.0	38.3 ± 1.9	84.8 ± 4.2	-
10 mins	-	-	57.5 ± 2.9	-
30 mins	8.3 ± 0.4	21.6 ± 1.1	29.3 ± 1.5	-

Note: The Galai particle size equipment operates to 95% confidence levels.

Table. 7.4 - Average sugar grain size (μm) with respect to time, solvent and mode of sonication.

VEGETABLE OIL				
	Icing Sugar		**Granulated Sugar**	
TIME	Probe	Tube	Probe	Tube
0 mins	55.0 ± 2.8	55.0 ± 2.8	1000 ± 50	1000±50
1 min	55.2 ± 2.8	51.0 ± 2.6	-	-
5 mins	43.0 ± 2.2	40.8 ± 2.0	-	-
30 mins	40.8 ± 2.0	40.6 ± 2.0	49.3 ± 2.5	-
60 mins	-	29.0 ± 1.5	30.2 ± 1.5	-

Note: The Galai particle size equipment operates to 95% confidence levels.

CONCLUSION

Problems were encountered with the dispersion of granulated sugar within the tube reactor and readings could not be obtained for dimethylformamide or vegetable oil.

Icing sugar was still fine enough to remain afloat dispersed within the solvent and particle size reduction was observed with the tube reactor for both dimethylformamide and vegetable oil.

Probe sonication effectively reduced particle size in dimethylformamide and vegetable oil for both icing and granulated sugars.

A greater particle size reduction was observed in dimethylformamide.

7.4 EFFECT OF ULTRASOUND ON SUGAR CRYSTALLISATION

7.4.1 INTRODUCTION

To be able to control the point at which crystallisation occurs would be a great advantage in any large scale production process. Often unwanted crystallisation occurs simply due to a slight drop in temperature or pressure within the pipeline. This could produce crystal growth within the pipes carrying the saturated solution resulting in possible blockages consequently halting production. This is clearly a great disadvantage in a continuous process. On the other hand if trying to initiate crystallisation problems may occur due to several factors such as the temperature, pressure or viscosity not being quite appropriate. Initiation of crystallisation may require a long 'lead in' time and this all results in a slow process. In the particular case of sugar refining, inducing crystallisation is particularly important.

Sugar from sugar cane was first produced in the Near East and Egypt in the late Middle Ages but large scale production was not developed until the 17th to 18th Centuries[93,94]. Nowadays refined sugar containing mainly sucrose is produced in the following manner:

SUGAR CANE
Shredded and Expressed

SUGAR LIQUOR (13-14% sucrose)
$Ca(OH)_2 + CO_3^{2-}$

$CaCO_3$ + REFINED SUGAR LIQUOR
Concentration of liquor in vacuum evaporators

CONCENTRATED LIQUOR
High Speed Centrifuging

RAW SUCROSE CRYSTALS
(to be further refined and purified)

Controlling the crystallisation rate and the crystal size would be a great advantage in the confectionery industry as these factors determine the quality of many products eg. fondants and fudges require many small crystals whilst for boiled sweets a glassy non-crystalline state is required. Inducing crystallisation efficiently and effectively at an exact point in the manufacturing process would also produce great advantages in the processing and handling of such materials and products.

CRYSTALLISATION

Crystallisation is a very complex area and many factors can influence the rate of crystallisation and the resultant size and uniformity of the crystals.

In supersaturated solutions clusters of molecules are constantly forming and reforming. At a specific size of the cluster, known as the critical nucleus, a choice is available. The nucleus may redissolve via loss of molecules or it may grow further through molecular collisions. If the choice is made to grow in size the critical point is passed and the nucleus can now grow to produce a crystal. Crystal growth takes place as the molecules of the compound are laid across the surface of the crystal in layers, with different faces growing at different rates. Factors such as concentration, temperature, purity, agitation and rate of cooling affect the rate of crystallisation and the resultant crystal form.

A solution which holds more than its saturation level of sucrose may spontaneously form crystals. Crystallisation can also occur if the solution has been 'seeded' with fine crystals or because foreign particles such as dust have acted as nucleation sites. Seeding is particularly important in the manufacture of sugar confections and the extent of crystallisation depends upon the degree of supersaturation and the amount of seed that is added. The larger the number of seeds the smaller the resultant crystals.

SONICALLY INDUCED AND ENHANCED CRYSTALLISATION

Sonication is believed to enhance both the nucleation rate and rate of crystal growth in a saturated or supercooled medium. There are thought to be two types of mechanism involved in sonically enhanced crystallisation. The first is called homogeneous crystallisation in which cavitation produces fresh nucleation sites in the medium. The second type called heterogeneous crystallisation involves the mechanical effect of cavitation which breaks up crystals to generate new small 'seeds' for further crystallisation.

Homogeneous Crystallisation

Hunt and Jackson[95] observed cavitation in a pure supercooled melt and noted that crystallisation/ nucleation occurred after the collapse of the cavitation bubble. It was suggested that the localised high pressures formed during cavitational collapse maybe strong enough to increase the melting point of the melt thus initiating nucleation.

Chormonov[96] investigated the effects of sonication on several supersaturated solutions such as thymol. He concluded that sonication induces spontaneous crystallisation via the formation of fresh nuclei.

Danilov[97] purified a melt solution of o-chloronitrobenzene via recrystallisation and concluded that fresh nuclei arise spontaneously within the melt when it is close to the metastable point.

Heterogeneous Crystallisation

Kapustin[98] reported that ultrasound affects crystallisation in a heterogeneous manner by producing many fresh nuclei from any seeds present. He observed small particles breaking off a thymol crystal when it was suspended into a saturated mixture of thymol and water and subjected to sonication, crystallisation in the absence of sonication did not occur. Sokolov[99] also found that sonicating a seeded solution of sugar and $ZnSO_4$ resulted in an increase in rate of crystallisation.

Van Hook et al[100] suggested that purification and removal of all possible nuclei from a solution of sucrose does not result in an acceleration of crystallisation rate when the solution is subjected to sonication, assuming that more effective cavitation is obtained on the removal of all possible contaminants. This suggests that in the case of sucrose solutions a heterogeneous mechanism is most likely. The possibility of obtaining a seed free solution of sucrose during normal manufacturing conditions is minimal and this theory does not therefore present any real practical problems. Sonication is thought to simultaneously enhance nuclei generation and crystal growth by taking advantage of the seeds already present in the solution.

SUCROSE AND GLUCOSE SYRUPS

A range of sugars are used within the confectionery industry. These include sucrose, glucose syrups, invert sugars and many others.

Sucrose (cane/ beet sugar) is a single sugar however glucose syrup contains a mixture of dextrose, maltose and a range of complex sugars. It is usually categorised by its free reducing sugar content and is labelled Dextrose Equivalent (DE) for example 69DE, will have 69% of the sweetness level of 100% dextrose. Invert sugar is a mixture of dextrose and fructose.

Sweets that contain a high level of sucrose may crystallise during manufacture or on standing. To avoid this problem the sugar content can be lowered to below 75% but unfortunately under these conditions the product becomes prone to mould. This can be avoided by the addition of glucose syrup or invert sugars which inhibit crystallisation but increase the level of sugar in the product. For example at 20°C a pure solution of sucrose can hold only 67% solids but gradual additions of invert sugar can increase this amount. There is however a limiting value, 52% solids, to the amount of invert sugar that can be added to a sucrose solution above which the total solids content will decrease. Dextrose will not crystallise from a solution which contains no crystals of the dextrose monohydrate, until the concentration is over 150% solids content. On the other hand sucrose will crystallise readily from solution.

Mixtures of different sugars are the norm rather than the exception in the confectionery industry resulting in very complex solutions.

7.4.2 EXPERIMENTAL CONDITIONS

Experimental conditions were followed as stated in section 2.7.

7.4.3 ANALYSIS CONDITIONS

A Shimadzu UV 2100 UV/Visible spectrophotometer was employed. The spectra were run on a % light transmission basis which when the cell was empty registered 100%. As the extent of crystallisation increased the amount of light reaching the detector decreased and the difference was plotted. The spectra were plotted over 20 hours at 700nm wavelength employing 1cm glass cuvettes/ cells in a cell holder maintained at 60°C.

7.4.4 RESULTS/DISCUSSION

Crystallisation Cell Temperature

The rate of cooling of a supersaturated solution will determine the amount and the size of the resultant crystals. If a slow cooling rate is maintained large crystals are formed as few nuclei are present and crystal growth along the faces of the seeds present is encouraged. If the temperature is dropped quickly many nuclei/ seeds form resulting in the production of many fine crystals. This is true for low viscosity solutions.

A number of other factors can come into play if the saturated solution is very viscous, as is the case with a saturated solution of sucrose. Reducing the temperature of the solution results in a loss of mobility and many nuclei/ seeds present in the solution may be thought of as being in a "frozen" state due to the viscous nature of the solution which reduces the amount of molecular collisions and therefore inhibits crystal growth. By maintaining a higher crystallisation temperature the 'mobility' of the molecules is increased within the solution and the rate of crystallisation increases.

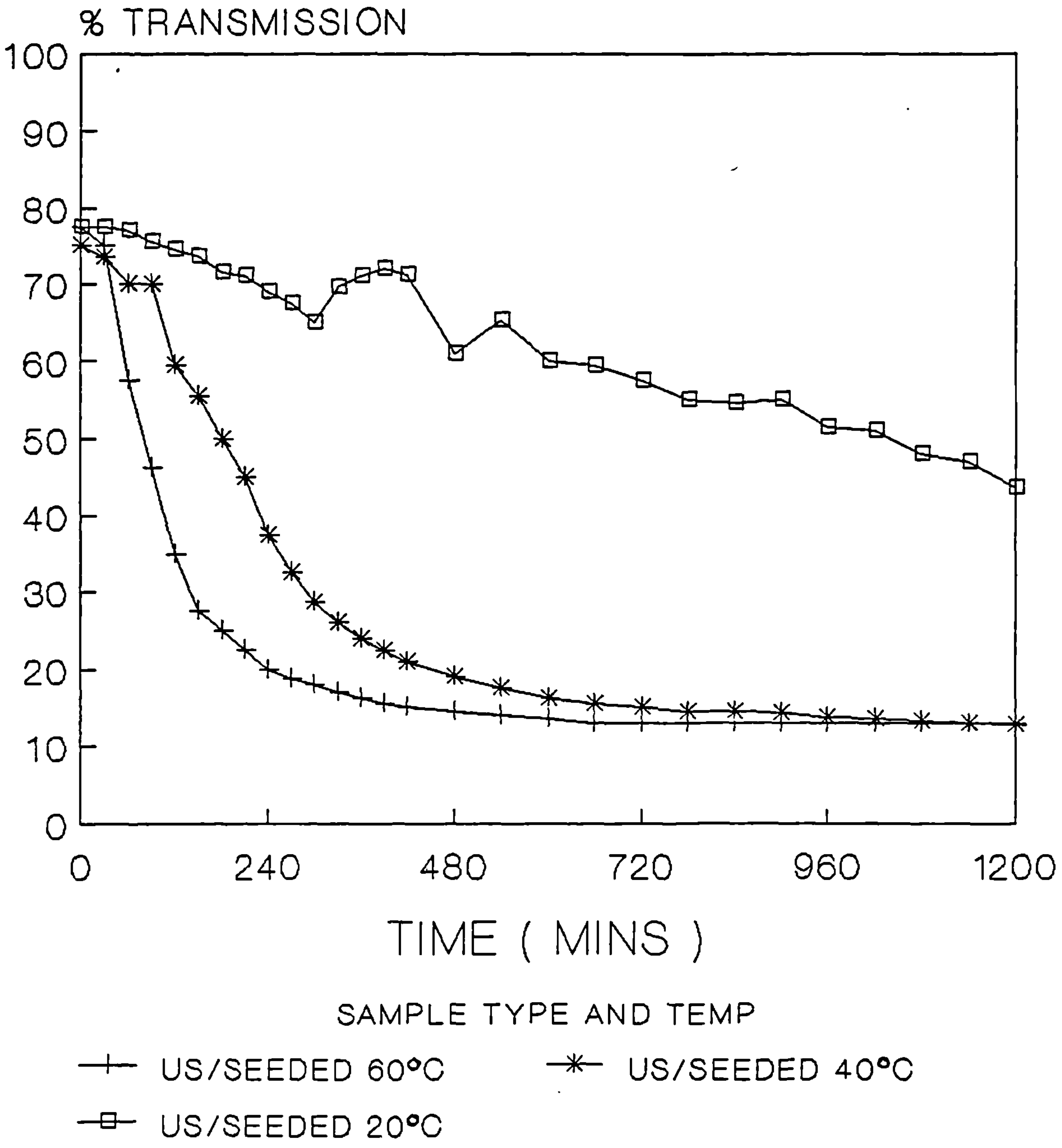
This phenomenon is shown in Table. 7.5 and Fig. 7.11 where the rate of crystallisation of an 80% solids solution of sucrose was monitored over a period of 20 hours at three different cell temperatures, namely 60°C, 40°C and 20°C.

The fastest rate of crystallisation was observed at 60°C followed by the sample maintained at 40°C. The rate of crystallisation at 20°C showed a large amount of fluctuation. This was probably due to room temperature changes as the temperature of the crystallising cell was quite low and these effects would be more pronounced.

Table. 7.5 - Crystallisation of an 80% solids solution of sucrose at different temperatures.

	% TRANSMISSION OF LIGHT		
TIME (mins)	**20°C**	**40°C**	**60°C**
0	77.5	75.0	77.5
30	77.5	73.5	75.0
60	77.0	70.0	57.5
90	75.5	70.0	46.25
120	74.5	59.5	35.0
150	73.5	55.5	27.5
180	71.5	50.0	25.0
210	71.0	45.0	22.5
240	69.0	37.5	20.0
270	67.5	32.5	18.75
300	65.5	28.75	18.0
330	69.5	26.0	17.0
360	71.0	24.0	16.25
390	72.0	22.5	15.5
420	71.25	21.0	14.5
480	61.0	19.0	14.0
540	65.25	17.5	13.5
600	60.0	16.25	13.0
660	59.5	15.5	13.0
720	57.5	15.0	13.0
780	55.0	14.5	13.0
840	54.5	14.5	13.0
900	55.0	14.25	13.0
960	51.5	13.75	13.0
1020	51.0	13.5	13.0
1080	48.0	13.25	13.0
1140	47.0	13.0	13.0
1200	43.75	12.75	13.0

Fig 7.11 - Crystallisation of an 80% solids solution of sucrose at different temperatures



VARYING CELL TEMPERATURE

Investigation into the Effects of Sonication

For the purpose of these experiments % crystallisation was noted by the amount of transmitted light passing through a glass cuvette filled with sugar solution. The end point of this experiment was taken to be the absence of any transmitted light which indicated that crystal growth had reached levels which prevent the passage of light through the cuvette. However this does not mean that total crystallisation has been reached within the whole solution only that crystallisation had reached within the limit set for this experiment.

An 80% solids solution containing only sucrose was prepared by dissolving 80g of sucrose into 20cm^3 of distilled water and heating it up to its boiling point. The solution cleared and when there was no evidence of undissolved sugar crystals it was treated in several ways, (Table. 7.6 and Fig. 7.12).

After dissolution the solution was poured into a glass cuvette and placed into a UV/ Visible spectrophotometer into a thermostatted cell maintained at 60°C. The formation of crystals was observed by the decrease in transmitted light, as above.

1) The slowest rate of crystallisation was observed for an unseeded non-sonicated solution of sucrose. After 14 hours approximately 70% crystallisation, that is 30% light transmission, was observed.

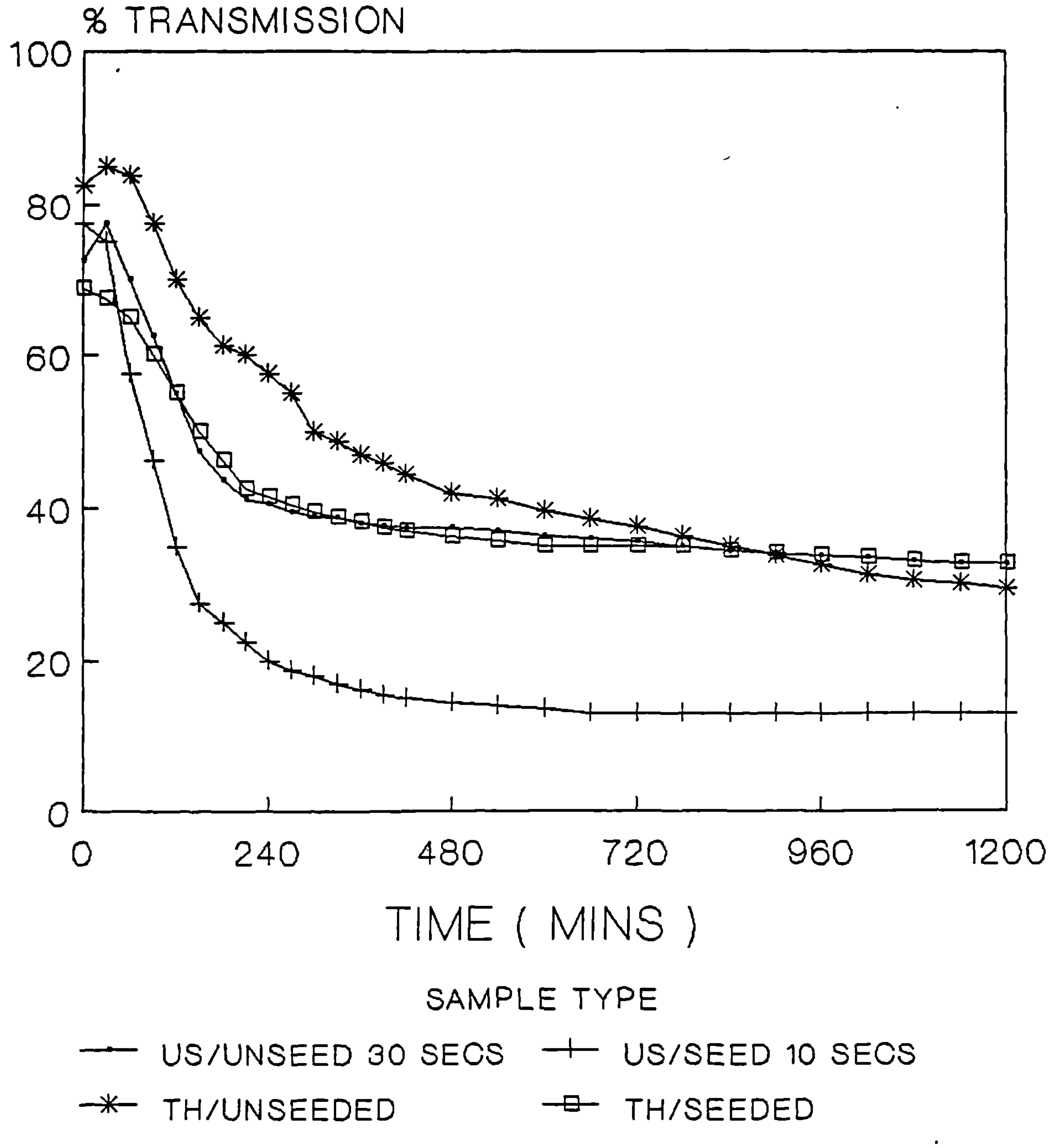
2) Seeding the non-sonicated solution resulted in a faster rate of crystallisation with the final amount being 70% crystallised but this was reached at the shorter time of approximately 3.5 hours.

3) Sonicating an unseeded solution of sucrose for 30 seconds gave a similar result to the seeded non-sonicated sample and indicated a slight advantage over the unseeded non-sonicated sample.

Table. 7.6 - % Light transmission, at 700nm, of an 80% solids solution of sucrose at 60°C.

TIME (mins)	**Sonicated 30 secs unseeded**	**Sonicated 10 secs seeded**	**Thermal unseeded**	**Thermal seeded**
0	72.5	77.5	82.5	68.75
30	77.5	75.0	85.0	67.5
60	70.0	57.5	83.75	65.0
90	62.5	46.25	77.5	60.0
120	55.0	35.0	70.0	55.0
150	47.5	27.5	65.0	50.0
180	43.75	25.0	61.25	46.25
210	41.25	22.5	60.0	42.5
240	40.63	20.0	57.5	41.5
270	39.5	18.75	55.0	40.5
300	39.0	18.0	50.0	39.5
330	38.75	17.0	48.75	38.75
360	38.13	16.25	47.0	38.18
390	37.75	15.5	46.0	37.5
420	37.5	15.0	44.5	37.0
480	37.5	14.5	42.0	36.25
540	37.0	14.0	41.25	35.63
600	36.25	13.5	39.5	35.0
660	36.0	13.0	38.5	35.0
720	35.5	13.0	37.5	35.0
780	35.0	13.0	36.25	35.0
840	34.38	13.0	35.0	34.38
900	34.0	13.0	33.75	34.0
960	33.75	13.0	32.5	33.75
1020	33.5	13.0	31.25	33.5
1080	33.0	13.0	30.5	33.0
1140	32.75	13.0	30.0	32.75
1200	32.75	13.0	29.5	32.70

Fig 7.12 - Comparison of crystallisation methods for an 80% solids solution of sucrose



CELL TEMPERATURE 60°C

4) The greatest effect was observed when a seeded sample was sonicated at high power, 40% output setting 8, for 10 seconds only. A even faster rate of crystallisation was observed with the final 87% crystallisation of the sample being reached after only 7 hours. 70% crystallisation was reached well within 2 hours, compared to 3.5 hours for the non-sonicated sample.

Although the samples were not specifically seeded it cannot be said that the samples were completely seed free. Dust and ultrafine nuclei were probably present and can cause the initiation of crystal growth. Elimination of these sources would require ultrafiltration, which would be extremely difficult with so viscous a liquid.

ADDITION OF GLUCOSE SYRUP

Glucose syrup is produced from the partial acid hydrolysis of starch thus resulting in a syrup which contains a mixture of sugar fragments such as dextrose, maltose and higher sugars. The degree of hydrolysis is determined by the amount of dextrose present and is quoted by the dextrose equivalent(DE) number. In this series of experiments a 69DE glucose syrup was employed.

By adding glucose syrup to a solution of sucrose the tendency of the solution to crystallise is decreased and the sugar content is increased, see earlier. The effects of varying the amounts of glucose syrup added to sucrose solution were monitored.

Initially a solution of 70g sucrose and 10g glucose in 10cm^3 of water was prepared, seeded and sonicated for 10 seconds before being poured into a cuvette and placed into the UV/ Visible spectrophotometer. All solutions were seeded and sonicated for 10 seconds only, simply because of the previous advantageous results, it is also impossible to state that a solution is unseeded and by seeding it deliberately you can categorically state that it is seeded.

The light beam of the spectrophotometer passes through the centre of the cuvette cell and any crystals formed will disrupt the progress of this beam and are registered by the detector. Unfortunately the UV/ Visible spectrophotometer did not register any sign of crystal growth for this sucrose/ glucose sample. However on removal of the cuvette it was noted that crystal growth had occurred but this was towards the base of the cuvette cell. If the cuvette cell was raised in its holder the detector light beam could be passed through the cell at a height of approximately 0.5cm from its base so that any crystal growth occurring in this area could be monitored. It was decided to adopt this procedure for these measurements.

80% Solids Solution

A solution containing only 80% sucrose reaches 93% crystallisation, 0.5cm from the cell base, within 1 hour from the sonication time, see Table. 7.7 and Fig. 7.13.

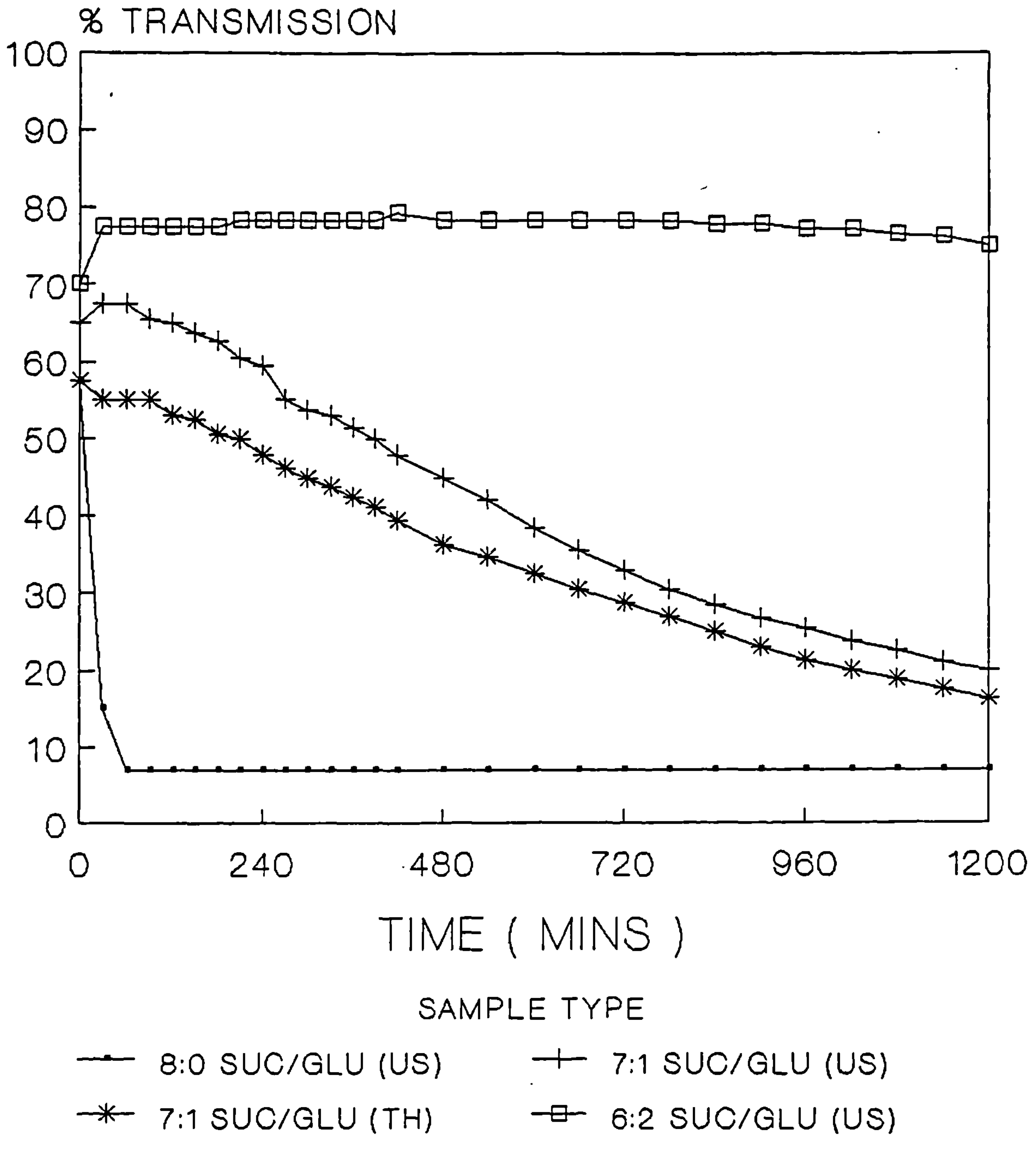
Progressive additions of glucose decreased the rate of crystallisation considerably. This solution of 70g sucrose and 10g glucose reached only approximately 85% total crystallisation after 20 hours and a solution of 60g sucrose and 20g glucose showed very little crystallisation even after 20 hours.

It was interesting to note that the rates of crystallisation of sucrose solutions containing glucose were unaffected by ultrasonic irradiation.

Table. 7.7 - Crystallisation of an 80% solids solution of sucrose/glucose mixture at 60°C.

	% TRANSMISSION OF LIGHT			
TIME (mins)	Sucr/Gluc 6:2 (US)	Sucr/Gluc 7:1 (Th)	Sucr/Gluc 7:1 (US)	Sucr/Gluc 8:0 (US)
0	70.0	57.5	65.0	57.5
30	77.5	55.0	67.5	15.0
60	77.5	55.0	67.5	7.0
90	77.5	55.0	65.5	7.0
120	77.5	53.0	65.0	7.0
150	77.5	52.5	63.75	7.0
180	77.5	50.5	62.75	7.0
210	78.5	50.0	60.5	7.0
240	78.5	48.0	59.5	7.0
270	78.5	46.25	55.25	7.0
300	78.5	45.0	53.75	7.0
330	78.5	43.75	53.0	7.0
360	78.5	42.5	51.5	7.0
390	78.5	41.25	50.0	7.0
420	79.5	39.5	48.0	7.0
480	78.5	36.25	45.0	7.0
540	78.5	34.75	42.0	7.0
600	78.5	32.5	38.5	7.0
660	78.5	30.5	35.5	7.0
720	78.5	28.5	33.0	7.0
780	78.5	27.0	30.5	7.0
840	78.0	25.0	28.5	7.0
900	78.0	23.0	26.75	7.0
960	77.25	21.25	25.5	7.0
1020	77.25	20.0	23.75	7.0
1080	76.5	18.75	22.5	7.0
1140	76.25	17.5	21.0	7.0
1200	75.0	16.25	20.0	7.0

Fig 7.13 - Crystallisation of 80% solids mixtures of sucrose/ glucose



CELL TEMPERATURE 60°C

85% Solids Solution

A solution containing only 85% sucrose solids seeded and crystallised almost instantaneously. A totally dissolved solution free of sugar granules could not be obtained and therefore no attempt was made to monitor this solution.

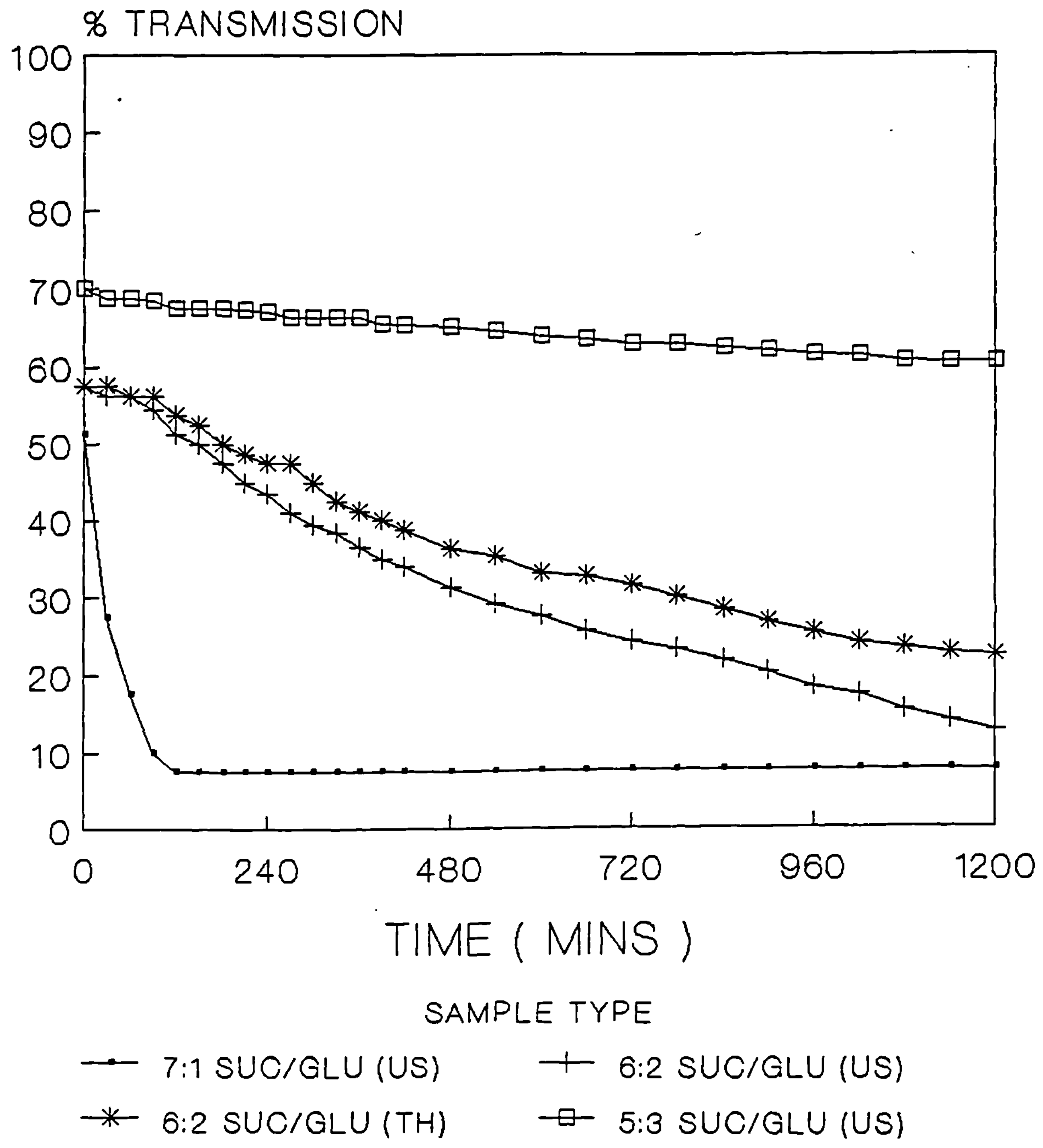
Addition of glucose syrup to the sucrose solution, in a sucrose to glucose ratio of 7:1, produced a sample which reached 93% crystallisation, 0.5cm from the base of the cell, within 2 hours from the sonication time, see Table. 7.8 and Fig. 7.14.

Progressive additions of glucose again decreases the rate of crystallisation considerably. A solution containing 85% solids consisting of sucrose and glucose in the ratio of 6:2 reached only approximately 85% total crystallisation after 20 hours and a solution with a sucrose to glucose ratio of 5:3 showed little sign of crystallisation even after 20 hours. As in the previous example (80% solids) the rates of crystallisation of non-sonicated and sonicated sucrose/ glucose mixtures appeared to be similar.

Table. 7.8 - Crystallisation of an 85% solids solution of sucrose/glucose mixture at 60°C.

	% TRANSMISSION OF LIGHT			
TIME (mins)	**Sucr/Gluc 7:1 (US)**	**Sucr/Gluc 6:2 (Th)**	**Sucr/Gluc 6:2 (US)**	**Sucr/Gluc 5:3 (US)**
0	51.25	57.5	57.5	70.0
30	27.5	57.5	56.25	68.75
60	17.5	56.25	56.25	68.75
90	10.0	56.25	54.5	68.5
120	7.5	53.75	51.25	67.5
150	7.5	52.5	50.0	67.5
180	7.5	50.0	47.5	67.5
210	7.5	48.75	45.0	67.25
240	7.5	47.5	43.5	67.0
270	7.5	47.5	41.0	66.25
300	7.5	45.0	39.5	66.25
330	7.5	42.5	38.5	66.25
360	7.5	41.25	36.5	66.25
390	7.5	40.0	35.0	65.5
420	7.5	38.75	34.0	65.25
480	7.5	36.25	31.25	65.0
540	7.5	35.25	29.0	64.5
600	7.5	33.0	27.5	63.75
660	7.5	32.5	25.5	63.25
720	7.5	31.25	24.0	62.5
780	7.5	29.75	23.0	62.5
840	7.5	28.0	21.5	62.0
900	7.5	26.5	20.0	61.5
960	7.5	25.0	18.0	61.0
1020	7.5	23.75	17.0	60.75
1080	7.5	23.0	15.0	60.0
1140	7.5	22.25	13.75	59.75
1200	7.5	22.0	12.5	59.75

Fig 7.14 - Crystallisation of 85% solids mixtures of sucrose/ glucose



CELL TEMPERATURE 60°C

Comments on the Apparent Similarities between Sonicated and Non-sonicated

Samples containing Glucose

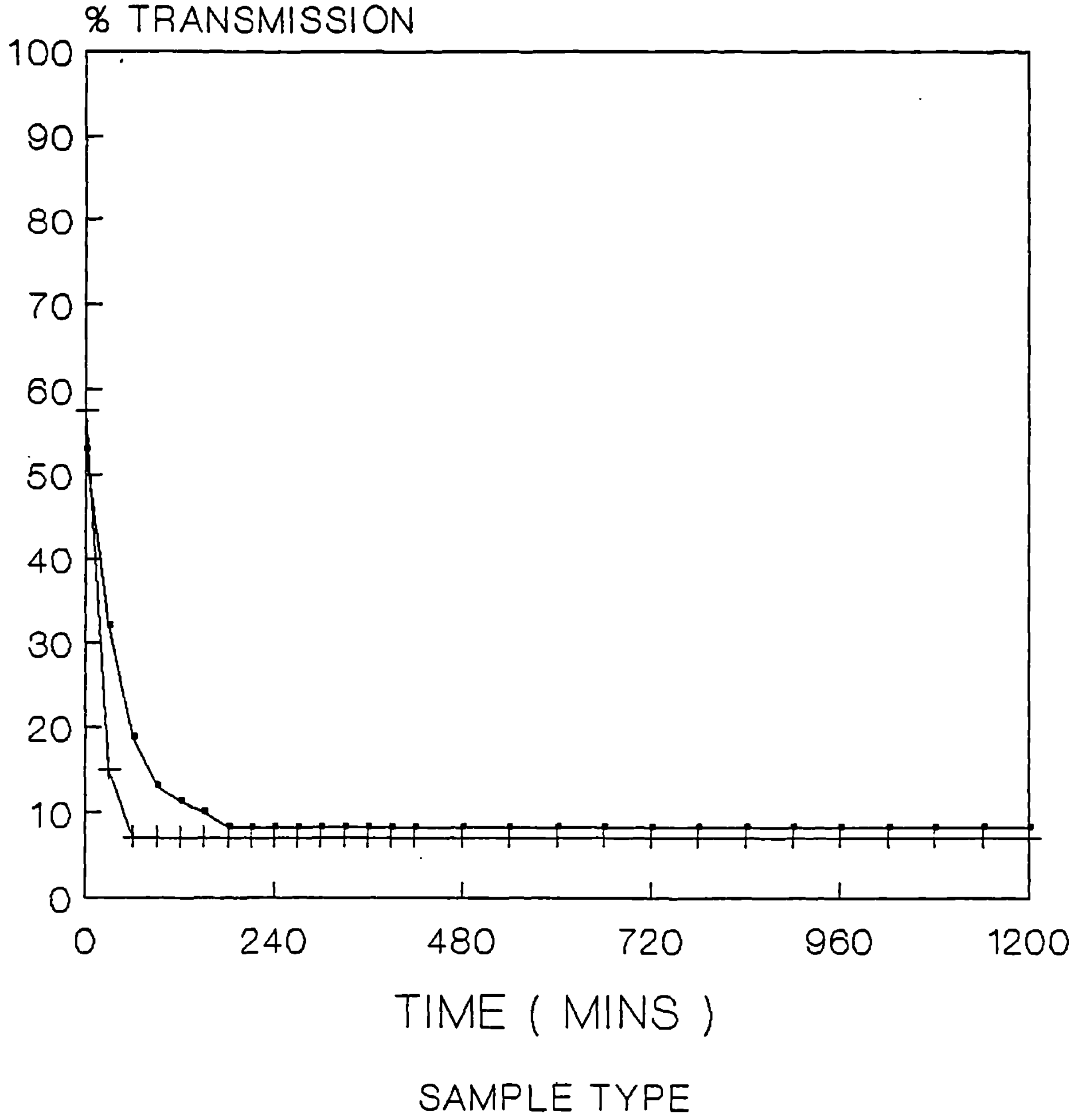
It had been noted that when observing light transmission near the base of a cuvette cell for signs of crystallisation it was not possible to detect differences between sonicated and non-sonicated samples. Crystallisation initially begins at the base or on the inside surface of a vessel and as the extent of crystallisation increases growth towards the centre of the vessel begins. Efficiency of crystallisation can be observed as the rate at which centre crystal growth proceeds. This is quite satisfactory in the case of pure samples of sucrose as crystallisation proceeds very efficiently and can be easily monitored at the cuvette centre. On the addition of glucose syrup however the reduction in rate of crystallisation also slows crystal growth towards the centre of the vessel and thus prevents efficient monitoring by the UV/Visible spectrophotometric method employed.

Observation of the crystallisation of two samples towards the base of the cuvette which are known to crystallise at varying rates at the cuvette centre allows a determination of whether there is a difference in the sonicated and non-sonicated rates of the glucose solutions or if in fact it cannot be monitored. An 80% solids solution of pure sucrose was seeded and sonicated for 10 seconds and the rate of crystallisation 0.5cm from the base of the cuvette cell, rather than the centre, was observed, see Table. 7.9 and Fig. 7.15. This sample reached 93% crystallisation within 1 hour. When compared to a similar non-sonicated seeded solution 93% crystallisation was reached within 3 hours.

Table. 7.9 - Crystallisation of an 80% solids solution of sucrose in an attempt to determine the efficiency of analysis 0.5cm from the base of the cuvette.

% TRANSMISSION OF LIGHT		
TIME (mins)	**Thermal - seeded**	**Sonicated - seeded**
0	53.0	57.5
30	52.0	15.0
60	18.75	7.0
90	13.0	7.0
120	11.25	7.0
150	10.0	7.0
180	8.3	7.0
210	8.3	7.0
240	8.3	7.0
300	8.3	7.0
360	8.3	7.0
420	8.3	7.0
480	8.3	7.0
540	8.3	7.0
600	8.3	7.0

Fig 7.15 - Crystallisation of 80% solids solution of sucrose in an attempt to determine the efficiency of analysis



Samples 0.5cm from base of cuvette
CELL TEMPERATURE 60°C

Thus a slight difference in rate was observed however the results were not as striking as the comparable ones obtained at the centre of the cuvette, see earlier. It was thus not possible to conclude that addition of glucose interfered with the beneficial effects of the sonication of a seeded solution.

Time of Irradiation

Three 80% sucrose solutions were seeded and then sonicated for 5, 10 or 30 seconds, employing a 1.2cm diameter sonic probe with the Sonics and Materials equipment at setting 4 with 10% output. The rate of crystallisation was observed using the centre of the cuvette. Under these conditions no increase in rate or extent of crystallisation was observed and this would seem to indicate that increasing the time of sonication for a seeded saturated solution of sucrose does not necessarily increase the rate of crystallisation, see Table. 7.10.

TABLE. 7.10 - Crystallisation of sucrose with respect to the amount of ultrasonic irradiation applied.

	% TRANSMISSION OF LIGHT AND IRRADIATION TIME			
TIME (mins)	5 secs	10 secs	30 secs	Pulsed 10 secs
0	85.0	77.5	79.0	67.5
30	80.0	75.0	77.5	67.5
60	75.0	57.5	67.5	67.5
90	67.5	46.25	57.0	65.0
120	57.5	35.0	47.5	62.5
150	48.75	27.5	42.0	60.0
180	41.25	25.0	37.0	53.75
210	34.0	22.5	32.5	51.25
240	29.0	20.0	27.0	47.5
270	25.0	18.75	22.0	45.0
300	22.5	18.0	17.75	42.5
330	20.0	17.0	15.0	41.25
360	17.5	16.25	12.5	39.5
390	17.0	15.5	11.25	37.0
420	15.0	15.0	10.0	35.5
480	14.5	14.5	9.5	33.75
540	13.5	14.0	9.5	32.75
600	13.0	13.5	9.5	32.0
660	12.5	13.0	9.5	30.5
720	11.5	13.0	9.5	28.75
780	10.5	13.0	9.5	27.0
840	10.0	13.0	9.5	26.0
960	9.25	13.0	9.5	25.0
1020	8.75	13.0	9.5	23.75
1080	8.0	13.0	9.5	22.75
1140	7.75	13.0	9.5	21.25
1200	7.5	13.0	9.5	20.0

A further seeded solution of sucrose was sonicated via a 50% pulsed cycle of sonication for 20 seconds. This resulted in a slower rate of crystallisation with only 20% crystallisation observed. This seems to suggest that pulsed sonication may give enough time for any minute sugar particles formed, by the initial sonic wave, to re-dissolve into the hot sugar solution during the break before the following ultrasonic pulse.

7.4.5 CONCLUSION

In summary the greatest rate of crystallisation was observed at higher temperatures where the solution retains some of its mobility and thus allows crystal growth.

Seeding sucrose solutions increased the rate of crystallisation and application of ultrasound to a seeded solution increased the rate of crystallisation still further.

Addition of glucose to sucrose solutions, although still retaining the sugar content, reduced the rate of crystallisation. Due to the method of analysis employed for glucose solutions application of sonication appeared to have little effect on crystallisation rate.

Finally, increasing the time of sonication of a seeded solution appeared to have little effect on the overall rate of crystallisation.

CHAPTER 8

ULTRASOUND IN THE PREPARATION OF CONFECTIONARY PRODUCTS

8.0 ULTRASOUND IN THE PREPARATION OF CONFECTIONERY PRODUCTS

8.1 EFFECT OF ULTRASOUND ON STARCH

8.1.1 INTRODUCTION

Many problems are associated with the large scale processing of food materials. The dispersion and/or solubilisation of powders into water is notoriously difficult simply due to the large volumes involved. It was hoped that sonication would enhance the rate at which the powders were incorporated into solution. This would reduce pre-mix times hence increasing the output of the process thus making it more efficient and economical. The biohazard risks associated with the handling of large quantities of materials would also be reduced.

Problems are also encountered in production due to the viscosity of the materials handled. Transportation problems often result in blockages in pipework and/or valves resulting in frequent dismantling and cleaning of the relevant parts. These problems all result in a reduction in output and production. A series of experiments were performed to determine if a temporary or permanent reduction in viscosity could be achieved by subjecting the sample to ultrasound. A temporary reduction in viscosity is a result of a reduction in intermolecular forces. This would allow easier flow of materials through pipework thus aiding processing and avoiding unnecessary blockages. A permanent reduction in viscosity is normally the result of intramolecular force reduction and usually refers to the degradation of the starch molecule itself.

Uses and Sources of Starch

In the world starch is one of the major components of human diets. In the UK alone 32% of the average diet contained starch[101, 102] . In the world market maize starch represents a large proportion of commercial starch and starch is also derived from rice, sago and tapioca. Potatoes also have a high starch content and commercially this is also a large source of starch. Wheat starch is also an increasingly important source of starch. The other valuable wheat product, wheat gluten, is rich in protein and is used to supplement low protein flours.

Starch is composed mainly of two components, Amylopectin and Amylose, however the large diversity of maize products allows for the existence of many different starch compositions. <u>Corn starch</u> contains 73% Amylopectin and 27% Amylose whereas <u>waxy maize</u> contains only Amylopectin and <u>amylomaizes</u> contain upto 80% Amylose. Each starch has specific properties and thus specific uses.

Of the whole world production of starch: 27% is used in the paper, packaging and textile industries, obtained mainly from potato starch. Most of the maize starch is used in the food and drink industries and is employed as starch thickeners for sauces, custards and the like, it is also used in the drinks and confectionery industries as glucose, maltose and fructose syrups.

Derivatised and Modified Starches

Natural starches are often converted to derivatised products to maximise their potential. Often specific properties are displayed which can pinpoint the areas for maximum commercial use. The amount of chemically altered starches used within the food industries is now being monitored closely and so often, rather than have the materials undergo extensive toxicological examinations, it can be more economic to limit their use.

Introducing chemical modifications to the polysaccharide chains will alter their interactions. Thus oxidation, alkylation or esterification of the glucose hydroxyl groups of the polysaccharide will affect the hydrogen bonding, charge interactions and hydrophobic characteristics of the whole molecule.

In addition to these minor modifications it is also possible to synthesise alternate polymeric materials from a starch basis. Examples of these are biodegradable polymers from derivatised starches, biodegradable detergents from esterified starches and rubber substitutes from starch xanthates. It is also possible to produce low molecular weight materials via hydrolysis with enzymes or acid hydrolysis followed by enzyme attack. This breakdown of the large starch polymer chains provides glucose syrups which can be fermented to give ethanol or isomerised to give fructose.

Starch Composition and Structure

As stated previously starch consists mainly of two components:

Amylose which has a molecular weight somewhere between 10^5 - 10^6 with approximately 500 - 5000 glucose unit chain lengths connected via α-(1 -> 4) glucan linkages. It is a fairly linear polymer with a slight amount of branching, indicated by the incomplete hydrolysis of the molecule by the enzyme α-amylase which specifically attacks the α-(1 -> 4) linkages. There is thought to be 2->8 branches per molecule with side chain lengths between 4->100 glucose units.

Amylopectin has a molecular weight somewhere between 10^7 - 10^9. It has a tree-like structure with a short chain linear structure of the α-(1 -> 4) glucan type with approximately 5% branching occurring of the α-(1 -> 6) linkage type. The degree of polymerisation for the branched chains is 15 units for the A-type chains and 45 units for the B-type chains.

Starch is a semi-crystalline molecule. Evidence suggests that it is the amylopectin chains that are responsible for this crystallinity. This is confirmed by the fact that waxy-maize starches exhibit crystallinity and they do not contain amylose. Also amylose may be leached out of starch granules without affecting their crystallinity. The structure of the amylopectin chains is thought to be double helical with a high degree of hydrogen bonding between the polysaccharide chains. Although some degree of crystallinity exists approximately 70% of the starch granule is thought to be amorphous. Most of the amylose is found in the amorphous region together with a lot of the amylopectin in starches such as corn starch which contain only approximately 27% amylose. The exact physical state of this amorphous structure is unknown.

Gelatinisation of starch is the name given to the process of swelling of starch molecules and the disruption of any order within the molecule. Gelatinisation is a direct result of the breaking of the hydrogen bonds between the polysaccharide chains in the crystalline phase, and to a lesser extent in the amorphous regions, resulting in swollen amylopectin molecules. This leaves the polysaccharide chains more open to chemical or enzyme attack. Heating in the presence of water is the usual method for disruption of these bonds although the same result can be achieved at lower temperatures by use of solvents such as liquid ammonia or dimethylsulphoxide or mechanically by milling.

Retrogradation is the name given to the realignment of polymer chains and the accompanying loss of solubility. This is achieved when soluble amylose affects the viscosity of the aqueous phase in which the swollen amylopectin molecules are held. On cooling, the amylose chains will reassociate leading to retrogradation.

8.1.2 EXPERIMENTAL CONDITIONS

The cornflour mixture employed in all the experiments was prepared as in section 2.8.1.

8.1.2.1 STARCH GELATION

Thermal Reaction

Reaction conditions as quoted in section 2.8.1.1.

Sonicated Reaction Conditions

Reaction conditions employing the sonic probe system as quoted in section 2.8.1.2.

Reaction conditions employing the sonic bath system as quoted in section 2.8.1.3.

Reaction conditions employing the tube reactor system as quoted in section 2.8.1.4.

Microwave Conditions

Reaction conditions as quoted in section 2.8.1.5.

8.1.2.2 STARCH DEGRADATION

Degradation of Concentrated Starch

Reaction conditions as quoted in section 2.8.2.1.

Degradation of Gelled Starch

Reaction conditions as quoted in section 2.8.2.2. Within 5 minutes a reduction in viscosity was observed, in the case of amylopectin this was a permanent effect. For amylose the reduction was temporary but surprisingly in the case of cornstarch, which is a mixture of amylopectin and amylose, there was no reduction in viscosity at all. Alterations in viscosity were clear enough to be judged by the naked eye.

8.1.3 RESULTS/ DISCUSSION

8.1.3.1 INCREASING THE RATE OF MIXING AND GELATION

Custard gelation

As a confectionery product custard contains starch additives to aid thickening on heating. An investigation was undertaken into a possible enhancement in mixing of the custard powders, or a faster time of gelation, in the presence of ultrasound.

As a control, thermal gelation of custard was attempted for a series of temperatures and final results indicated that gelation did not take place much below 70°C.

Boiling Water - instantaneous gelation
80°C - gelation within 30 seconds
70°C - gelation within 1 minute 30 seconds
60°C - no gelation even after 1 hour

Sonication was then attempted with the high powered sonic probe. Probe settings at 8, 6 and 2 were used to vary the amount of power applied. Sonication at a constant 25°C produced no gelation therefore the temperature of the mixture was allowed to rise as sonication was applied.

Setting 8 - gelation within 6 minutes
Setting 6 - gelation within 10 minutes
Setting 2 - No gelation after 15 minutes

The major factor to be noted is that in all the sonicated experiments gelation occurred as 74°C was reached. The gelation time altered as the time of sonication necessary to reach the required gelation temperature increased with a power decrease, heating of the solution is less effective at lower powers. Thus at the low power setting of 2, 74°C was not attained after 15 minutes sonication and gelation did not occur. Gelation thus appears to be a totally thermal process and sonication does not affect its rate.

Dispersal of the powders however was quite efficient when employing the sonic probe system. At the higher powers of sonication, with no external interference, total solubilisation was obtained within 30 seconds at the lower power setting within 2 minutes. Gelation thus appears to be a thermal response but sonication clearly acts as an efficient dispersal/ solubilisation system.

An ultrasonic cleaning bath does not provide sufficient power for efficient mixing and solids dispersal. The powders remained undissolved after 5 minutes of unaided sonication. For this system gelation only occurred when a temperature of 74°C was attained.

When a glass tube, of diameter 26.5mm, was employed with the tube reactor, containing water at 80°C, solids dispersal was also very poor within the tube system. The powders tended to float to the surface of the immersed glass vessel. Nevertheless on sonication of this mixture a temperature of 70°C was reached in only 30 seconds suggesting efficient heat transfer. After 3.5 minutes a weakly gelled solution was obtained as most of the powders were not solubilised into the water. Pre-mixing of the powders is thus necessary before adding the mixture to the tube reactor.

Repeating the experiment with a pre-mixed solution resulted in efficient heat transfer and gelation occurring after 2.5 minutes. An unusual feature present is that the custard does not set above the level of sonication, that is outside the sonication zone. The level of custard within the glass vessel is slightly higher than the depth of the tube reactor itself.

Only the custard within the 32cm deep sonication area is exposed to sonication and thickens leaving a watery layer on its surface. The explanation may be that inefficient heat transfer to the surface of the custard is present and therefore the efficiency of gelation is reduced, the solution above the sonication zone being slightly lower in temperature.

Employing the tube reactor as a reaction vessel itself the custard was premixed and placed directly into the tube reactor. Sonication was applied and the temperature within the tube rose as follows:-

0 minutes - 15.1°C

5 minutes - 24.3°C

15 minutes - 35.1°C

30 minutes - 50.0°C

45 minutes - 67.3°C

70.0°C was attained after 48 minutes 15 seconds and gelation occurred between 52 minutes 45 seconds and 53 minutes 45 seconds at a temperature of 74.5°C. Again a thermal effect is present with gelation time dictated by the rate at which appropriate temperatures are reached.

An attempt was made to estimate the efficiency of microwave irradiation on gelation. The custard mixture exposed to microwave irradiation underwent gelation as 70°C was approached but the heat distribution was non-uniform. The surface retained heat more efficiently than the bulk solution, and thus to ensure efficient heat distribution and a more uniform gel mechanical mixing would be required.

Temperature changes within the custard were as follows:-

10 sec - 24°C - liquid

20 sec - 34°C - liquid

30 sec - 42°C - liquid

40 sec - 49°C - liquid

50 sec - 57°C - liquid

60 sec - 60°C - solidification at surface

70 sec - 69°C - further surface solidification

80 sec - 68°C - totally gelled

The custard took longer to gel under these conditions as microwave irradiation was applied only in 10 second bursts to allow for stirring. Once again gelation appears to be a thermal response.

Cornflour gelation

Custard powder is a blend of several materials such as cornstarch, food colourings and emulsifiers. These additives could affect the way cornstarch acts under thermal and sonicated conditions. It was thought necessary to repeat the experiments with unadulterated cornflour. Cornflour contains cornstarch to aid thickening however the exact composition of the cornstarch was not confirmed, see later.

Thermal gelation was attempted at a series of temperatures and final results indicated that gelation did not take place much below 70°C.

Boiling Water - instantaneous gelation
80°C - gelation within 10 to 20 seconds
70°C - gelation within 1 minute 45 seconds
60°C - no gelation even after 1 hour

Here results are similar to those obtained with custard powders.

Sonication was then attempted with the high powered sonic probe at high and low temperatures. The temperature within the solution, starting at room temperature, was allowed to rise under sonication and reached 67.8°C after 9 minutes 45 seconds when thickening began. Gelation was complete at 10 minutes 35 seconds. Here again a thermal gelation response appears to be present. Sonication was then attempted at low temperatures and the cornflour mixture was irradiated for 15 minutes in an ice bath and then placed in an 80°C water bath. Gelation began as 70°C was reached and was complete within 2 minutes. This would seem to indicate that cornflour cannot be gelled at lower temperatures and pre-sonicated cornflour shows no improvement over conventional mixing before thermal gelation.

Cornstarch gelation

The precise content of commercial cornflour was unknown and therefore cornstarch itself was used. The cornstarch employed in these experiments contained 75% Amylopectin and 25% Amylose.

Thermal experiments performed as controls indicated that gelation began at 68°C and was complete in 30 seconds at 72°C. Probe sonication had no significant effect on this thermal response since once again gelation only occurred as 68°C was reached.

8.1.3.2 STARCH DEGRADATION

Gelation of starch appears to be a predominantly thermal process. The starch molecules become swollen as they absorb water and the intramolecular and intermolecular forces are reduced. Somewhat surprisingly sonication, under the conditions employed, does not appear to enhance this process. Starch is a long chain natural polymer and would be expected to behave in a similar manner to other polymers in the presence of sonication. Polymer degradation in the presence of ultrasound is a well documented phenomenon. Gooberman[103] stated that the degradation of a polymer molecule in an ultrasonic field proceeds via a mechanical mechanism. This is based on the forces produced in the bulk solvent on cavitational collapse which are powerful enough to degrade polymers in the vicinity of the cavitation bubble. There will be a limiting molecular mass below which the polymer will not degrade and this occurs when the polymer chain is short enough to deform rather than break under cavitational collapse.

Lorimer et al[104] investigated the polymerisation and depolymerisation of N-vinylcarbazole. It was stated that depolymerisation was due to a random and unsymmetrical cleavage of the chain around the mid-point leading to two radical species. Recombination of the smaller fragments from such processes will lead to the formation of molecules with lower molecular masses than the original. Here again there will be a limiting size for the resulting material below which further degradation cannot occur. Results would seem to indicate that the end result of such degradation is a monodispersed material.

This work was continued with an investigation of the effects of sonication on the degradation of dextran[105], a poly-glucose molecule with α-(1 -> 6) linkages. Partial acid hydrolysis of dextran followed by fractionation is the usual method of reducing the relative molecular mass distribution of the sample and can be a lengthy process. Samples of aqueous solutions of dextran were sonicated for 8 hours, at varying temperatures and at varying powers. Aliquots were withdrawn at intervals and analysed by gel permeation chromatography.

The initial chromatogram indicated 4 mass fractions. After only 15 minutes sonication the highest mass fraction was reduced considerably in size indicating an increase in the amount of lower mass material in the sample. On continued sonication a narrowing of the polydispersity of the sample was observed. This was assumed to be the result of a combination of two factors; first the 'preferential' degradation of large molecular mass material in the sample and secondly the existence of a limiting size of polymer below which degradation via sonication does not occur.

Increases in applied power increased the rate of degradation but the converse applied for increases in temperature indicating that the degradation is cavitational rather than thermal.

Chen Szu et al[106] investigated the sonicated degradation of the polysaccharide molecule dextran in an effort to produce lower molecular masses without modifying the structure. After 5 minutes irradiation the average molecular mass was 142,000. With continuing irradiation this mass fell to 100,000 (15 minutes irradiation), 79,000 (30 minutes) and 50,000 (60 minutes). A less pronounced effect was observed on further irradiation. Sonication resulted in a reduction in the viscosity of the polymer sample and a reduction and narrowing of the polydispersity of the polymer molecules. It was also observed that as the concentration of the sample was increased the amount of degradation decreased.

Basedow and Ebert[107] investigated the degradation of polymers with molecular masses between 30,000 and 100,000. They discovered that the type of solvent employed plays a large part in the extent of degradation obtained. Degradation of the polymer increases as the polymer coil unwinds.

In our own studies an attempt was made to determine whether sonication could effectively degrade starch. Samples of cornstarch, a mixture of 75% Amylopectin and 25% Amylose, and pure Amylose and pure Amylopectin were used in this qualitative study.

Natural starch is of large molecular mass material, consisting of amylose and amylopectin, and consequently a large degree of intermolecular bonding is present. Addition of water to starch results in its absorbtion into the polymer 'network', and as a result the polymer begins to swell. This destroys any order within the starch as it becomes disrupted due to the separation of the polysaccharide chains, mainly amylopectin, and hence a reduction in intermolecular bonding occurs. Gelation occurs as the polymer 'network' becomes saturated with water.

As a consequence of the reduction in intermolecular bonding the polymer chains become more susceptible to degradation, whether it be thermal, chemical or sonochemical. A permanent loss in viscosity will occur due to degradation and the reduction in molecular mass of the material. A temporary loss is due to a reduction in intermolecular bonding which can be re-established when the ultrasonic irradiation is switched off.

Degradation of Concentrated Starch

Thermal gelation of a concentrated solution of cornstarch results in gelation of only some of the starch polymer molecules in the sample. Insufficient water is present to allow for a large reduction in the degree of inter/intramolecular hydrogen bonding and hence total polymer gelation. Sonication of a concentrated sample of gelled starch may result in some degradation of the polymer and thus prevent further re-gelation on the further addition of water.

Probe sonication of thermally gelled concentrated starch resulted in no observable loss of viscosity in the sample. Increasing the concentration of a polymer sample leads to a higher degree of polymer entanglement and intermolecular bonding. This leaves the individual polymer chains less open to degradation. It is more difficult to degrade concentrated polymer samples as an increase in concentration results in a decrease in degradation. In order to efficiently degrade a concentrated polymer sample higher levels of sonic power would need to be applied.

In this experiment no observable loss of viscosity does not automatically indicate that degradation has not occurred. If degradation of the swollen polymer fraction and destruction of the gel structure does occur the absorbed water would become released. The water may then either solubilise the new lower molecular mass material or it may become re-absorbed by undegraded polymeric fractions. Under these circumstances the overall viscosity of the sample would remain constant. Further addition of water resulted in gelation occurring with all samples of cornflour, cornstarch, soluble starch, amylopectin and amylose.

It may be concluded that the extent of crystallinity, and intramolecular and intermolecular bonding, within the starch molecule is so great that the polysaccharide chains are less open to degradation. If some degradation does occur there is still enough 'order' present within the starch to allow for further water absorbtion, swelling of the molecules and the subsequent disruption of intra/intermolecular forces as gelation occurs.

8.1.3.3 DEGRADATION OF GELLED STARCH SOLUTIONS

The addition of a larger volume of water to starch will increase the number of swelled polysaccharide chains present within the gelled sample and reduce the amount of intermolecular bonding. This will eventually lead to a low viscosity 'solution'. Observing any alterations in viscosity will determine if some degradation of starch has occurred.

Degradation of Cornstarch

The viscosity of the thermally gelled cornstarch samples were monitored before and after sonication with a sonic probe. There was no significant change in viscosity indicating that a large amount of degradation had not occurred. However the sonicated sample became transparent which indicated further solubilisation of the starch. An increase in the solubility of the starch suggests some formation of lower molecular mass material. The formation of lower molecular mass material is usually accompanied by a decrease in viscosity of the sample. Conversely an increase in the concentration of soluble material within a sample results in a increase in viscosity. For this system any degradation of the starch will be compensated for by an increase in solubility of the resultant material thus the overall viscosity remains constant.

Degradation of Amylopectin

Amylopectin is a highly branched molecule with a large degree of intermolecular bonding. Thermal heating of the amylopectin solution produced the expected gelation of the polymer structure. On further stirring and heating no loss in viscosity of the gel was observed (see soluble starch). Suggesting that the intermolecular hydrogen bonds are not reduced sufficiently to temporarily destroy the gel structure of amylopectin.

Repeating the thermal experiment in an attempt to gel the amylopectin by sonication were not fruitful. The sample was allowed to heat up by sonic power alone. It appears that sonication degrades the amylopectin sufficiently to prevent gelation occurring, even as the temperature increases above the gelation range, that is above 70°C.

Sonication of thermally pre-gelled Amylopectin produced a transparent pourable liquid, within 1 minute 30 seconds at a temperature of 40°C. This clearly indicates degradation has occurred and further that the ultrasonic degradation is not a thermal effect. On cooling to room temperature the sample remains liquid even after 24 hours. This confirmed that sonication produced degradation of the polysaccharide chains and some loss of intermolecular bonding.

Degradation of Amylose

A permanent reduction in viscosity, which would be indicative of the degradation of amylose, does not appear to occur under the experimental conditions employed.

Thermal gelation of amylose can be achieved although higher temperatures and longer heating times are required, up to 10 minutes at 92°C, when compared to amylopectin and cornstarch. Repeating the thermal conditions but allowing the sample to heat up via sonication alone did not result in gel formation. Sonication appears to break down the intermolecular hydrogen bonding present and gelation via sonication alone was not achieved possibly due to the high temperatures required and low degree of intermolecular bonding present. Unexpectedly on discontinuing sonication thickening occurred as the solution cooled. This suggests that as the temperature was raised the solubility of the starch within the sample increased. As the temperature dropped the viscosity increased indicating a re-alignment of intermolecular bonds.

Sonication of pre-gelled amylose produced an unusual result. On sonication a pourable liquid is obtained almost instantly indicating a low degree of intermolecular bonding. On discontinuing the sonication re-solidification occurs immediately as the molecules re-align and re-establish their weak intermolecular bonds. This appears to be a temporary reduction in intermolecular forces and not a permanent degradation of the starch molecule itself.

Thermal gelation of the amylose may produce a gel in which the individual polysaccharide chains have a much higher degree of separation, and therefore low level of intermolecular bonding, than that observed with, for example, swelled amylopectin. This may account for the instant viscosity reduction observed on sonication. As to the apparent absence of degradation observed with amylose the explanation may be found in the relative molecular mass of the polysaccharide chains, being 10^5 - 10^6. This molecular mass may be close to the lower limit of molar mass for polymer degradation, under the experimental conditions and equipment employed for this study, therefore degradation would not be expected to take place.

Degradation of Soluble Starch

The soluble starch obtained was acid hydrolysed therefore all the internal hydrogen bonding within the crystalline part of the starch molecule will be reduced and the solubility of the starch is increased. This starch exhibits different behaviour from either cornstarch or its separate constituents amylose and amylopectin.

This soluble starch thermally gelled at approximately 62°C. However on continuation of heating and stirring, a reduction in viscosity was noted and a pourable liquid was obtained as 75°C was reached. On cooling the mixture re-gels as 62°C was reached. This shows that heating produces a temporary reduction in inter/intramolecular forces. This is unusual as it occurs on simple application of thermal energy indicating that the inter/intramolecular forces must be weak.

On sonication with a probe gelation was not reached even at 85°C. On cooling of this sample gelation occurred on standing. This does not appear to be due to a permanent degradation of the starch molecule, as re-gelation would not occur, but could probably be attributed to a reduced interaction between starch molecules as sonication is applied, at the lower temperatures 62°C sonication may prevent inter/intramolecular interactions and it seems likely that thermal effects may take over as the temperatures increases above this.

8.1.4 CONCLUSION

1) An increase in concentration results in a decrease of the extent of degradation as none of the concentrated samples of starch exhibited degradation or a reduction in inter/ intramolecular forces. Dilution of the samples allows for swelling of the starch molecules and a reduction of the intermolecular forces of the sample thus 'exposing' individual polysaccharide chains to possible degradation.

2) A permanent reduction in viscosity indicative of the degradation of the highly branched amylopectin sample was observed.

3) A temporary reduction in viscosity was observed for amylose indicating a reduction in the intermolecular forces present in the sample.

4) A combination of the two samples, such as in cornstarch, 75% amylopectin and 25% amylose surprisingly resulted in no viscosity reduction. Degradation of the polymer molecules may be compensated for by an increase in the solubility of the newly formed lower molecular mass fractions.

5) Soluble starch provides an ideal example of the effects of a reduction of intermolecular forces. For this system these weak forces are reduced quite easily by the application of heat and/or sonication.

8.2 EFFECT OF SONICATION ON CARAMEL

8.2.1 INTRODUCTION

In large scale production the problem of mixing powders into water is a very large one. In the production of caramel, milk powder must first be added to water. Once solubilisation occurs the sugar syrups and fat are added and heating may begin. This presents a problem in the transport of materials. The transport of milk powder or water separately to the sugar syrup presents no problem. It is the transport of the combination of the milk powder and water, to give milk solution, which prevents possible biological hazards, as bacteria find milk an ideal growth medium.

One solution to this problem would be the elimination of water by direct addition of milk powder to the sugar syrup. Normally however this results in a very 'grainy' caramel due to the presence of large crystals. An alternative is to alter the order of addition of the powders, that is milk powder could be pre-mixed with the sugar and this then added to water. This would eliminate or reduce any biohazards since the ingredients would be all transported separately to the 'cooking' vat.

The second area to be investigated is the removal of water from the caramel mixture during the heating process. This usually takes approximately 30 minutes during which time the caramel browns due to the Maillard reaction. It was hoped that sonication would enhance the browning of the caramel and possibly increase the rate of water removal.

8.2.2 EXPERIMENTAL PROCEDURE FOR CARAMEL PRODUCTION

8.2.2.1 3:1 TOTAL SUGAR/ TOTAL WATER RATIO

RECIPE EMPLOYED

See Section 2.9.1

In the Presence of Water

As quoted in section 2.9.1.1 and 2.9.1.2. The samples were prepared thermally and also by initial sonication followed by thermal completion.

In the Absence of Added Water

The samples were prepared thermally at 113°C, 2.9.1.3, and also at 103°C, 2.9.1.1. Sample preparation by initially sonicating the caramel for 15 minutes followed by thermal completion was also attempted, 2.9.1.2, as was an attempt to produce caramel via sonication methods alone, 2.9.1.4.

8.2.2.2 5:1 TOTAL SUGAR/ TOTAL WATER RATIO

A series of further experiments were performed with a lower moisture content caramel.

RECIPE EMPLOYED

See Section 2.9.2.

In the Presence of Water

Thermal Preparation

As quoted in section 2.9.1.1

Addition of Milk Powder to Sucrose

Here the order of addition was altered reaction conditions were followed as quoted in section 2.9.2.1.

Sonicated Conditions

Low power reaction conditions were followed as quoted in section 2.9.1.2.

High power reaction conditions were followed as quoted in section 2.9.2.2.

In the Absence of Added Water

As quoted in section 2.9.1.3. The samples were prepared thermally at 113°C. Sample preparation by initially sonicating the caramel for 15 minutes followed by thermal completion was also attempted, section 2.9.1.2.

8.2.2.3 ADDITION OF MILK POWDER TO GLUCOSE SYRUP

In these sets of experiments milk powder was mixed directly with glucose syrup and stirred/ sonicated for 15 minutes after which the remaining ingredients were added.

RECIPE EMPLOYED

See Section 2.9.3.

The samples were prepared thermally at 113°C, section 2.9.3.1. Sample preparation by initially sonicating the caramel for 15 minutes followed by thermal completion was also attempted, 2.9.1.2.

8.2.2.4 7:1 TOTAL SUGAR/ TOTAL WATER RATIO

A batch of low water content caramel was prepared and heated mainly by the heat produced due to sonication by either the small sonic bath or the sonic probe.

RECIPE EMPLOYED

See section 2.9.4.

Note in this recipe the glucose syrup was first heated to 120°C to produce a 90% solids syrup.

Sonicated Conditions

Low power reaction conditions were followed as quoted in section 2.9.1.2.

High power reaction conditions were followed as quoted in section 2.9.2.2.

8.2.3 ANALYSIS PROCEDURE

The food industry uses "spread" as a measure of the fluid properties of the final sample. The "spread" (increase in area) of the caramel is measured at 40°C, which is equivalent to a hot summer day. Caramel spread is undesirable in confectionery products since it may result in an unattractive product and presentation is important in the 'market place'. The tendency for caramel to spread at higher temperatures must be controlled particularly in products such as Twix or Mars bars. A good caramel should exhibit very little or no spread at 40°C.

The method employed for monitoring caramel spread is as follows:-

The caramel was cooled and cut into a disk, 3cm diameter and 0.5cm depth, employing a 'pastry' cutter. It was then placed onto a thin sheet of glass and its boundaries marked with a waterproof thin tipped marker pen. The caramel was then placed into a 40°C oven and left for one hour after which the degree of 'spread' was marked *i.e.* the new boundaries of the caramel were marked. For a period of 3 hours this spread was marked hourly and the caramel was then left in the oven overnight and the boundary was re-marked 24 hours later. The caramel was removed from the oven and the glass sheet leaving 5 marked circles. The glass sheet was taken to a graphics tablet upon which the area within each circular marking can be determined with the use of a magnetic pen and a suitable computer programme thus enabling a determination of the degree of spread of the caramel from its original size.

8.2.4 RESULTS/DISCUSSION

8.2.4.1 Alternative Methodologies using a 3:1 Total Sugar/Total Water Ratio

In the Presence of Water

The basic caramel mixture with a total sugar/total water ratio of 3:1, when prepared entirely by thermal methods, resulted in a 5% increase in the total area of the caramel, 5% spread, which did not alter after 24 hours at 40°C. The resultant caramel exhibited brown colouration with very elastic properties and a long thread when pulled apart. These are the desirable properties which should be present in caramel.

Sonication of the reagents to induce efficient distribution of the powders within the water was examined. Milk powder was added to the water and sonication applied, via a sonic bath, for 5 minutes. This was followed by granulated sugar and fat, sonication was applied for 5 minutes after each addition. Finally the other constituents were added and the reaction completed thermally to 115°C. The resultant caramel exhibited 12% spread at 40°C after 24 hours. This was slightly inferior to the thermally prepared 'control' caramel sample indicating slightly less homogenisation of the constituents. The caramel exhibited a slightly grainy texture, suggesting incomplete solvation of the sugar granules within the caramel matrix resulting in the presence of large sugar crystals. After 24 hours at 40°C the caramel appeared to be slightly greasy indicating incomplete emulsification of the fat within the matrix.

In the Absence of Added Water

The thermal experiment was repeated in the absence of added water. Glucose syrup and fat were stirred and heated to 40°C to improve their mobility (both are solids at room temperature). Once the viscosity was reduced granulated sugar and milk powder were added to the mixture. This was heated and stirred at 300 rpm until 115°C was reached, this was attained very quickly as there was no water to remove from the system and the thermal capacity of a viscous liquid is much greater than the standard caramel mix. The caramel had to be removed from the heat before complete browning had occurred, as overheating results in a very brittle caramel, and so a pale caramel was obtained. The resultant caramel exhibited no spread at 40°C. An extremely grainy caramel was obtained indicating incomplete solvation of the sugar granules within the caramel matrix. The caramel was also very hard when prepared in the absence of added water, probably resulting from the incomplete solvation of materials, together with the possibility of solidification of the sugar granules into a more solid mass on cooling.

In an effort to reduce the 'hardness' of the caramel it was thought that keeping the caramel at the lower final temperature of 103°C would reduce the amount of water loss and increase its flexibility. The standard thermal reaction conditions but in the absence added of water were applied. This resulted in a very brittle caramel with a very grainy texture indicating that even at the lower temperatures employed insufficient water was present. Under these conditions there was insufficient time for browning to occur and a white caramel was obtained. On pouring the caramel onto waxed paper fat began to seep out of the caramel matrix indicating a poor degree of homogenisation.

A second experiment was attempted. This involved an initial 15 minute sonication of the caramel mixture which was then completed thermally, reaching the final temperature of 103°C. A very brittle caramel resulted indicating still too little water, probably the moisture contained within the glucose syrup added. Insufficient solvation of the sugar granules into the caramel matrix resulted in a grainy texture. A pale caramel was obtained also indicating insufficient time at high temperatures, approximately 100°C, to enable efficient browning to occur. Fat retention also appeared to be poor indicating insufficient homogenisation of the matrix.

Full sonication of the caramel mixture presented problems. The ingredients were added to a sonic bath and the temperature allowed to rise with sonication. 103°C was attained within 30 minutes but the temperature did not rise above this level. The low power of sonication supplied by the sonic bath was not sufficient enough to induce homogenisation of the materials and external stirring had to be applied occasionally to re-introduce the fat to the bulk of the caramel, the fat separated out of the bulk solution and floated to the surface. After 45 minutes the sample was removed from the sonic bath. Efficient browning had occurred as the high temperatures and the length of time at these temperatures were sufficient to allow the Maillard reaction to occur.

The resultant caramel mixture was separated into two halves. One half was cooled after 103°C was reached and the other half was transferred to a heating mantle where it was raised in temperature to 115°C to complete the reaction.

The 103°C caramel exhibited 36% spread within 1 hour at 40°C, 43% after 2 hours, 67.8% after 4 hours and 85% after 24 hours. The homogeneity of the sample was very poor. Although this sample exhibited the correct brown colouration it has a grainy texture indicating non solvation of the sugar into the caramel matrix. Due to the low temperature to which it was heated (only 103°C) the resultant caramel was also very soft, indicating poor water absorbance by the particles. This is completely opposite to the corresponding thermal reaction which produced a brittle caramel even at 103°C. Sonication may reduce the amount of water removed from the system. The Maillard reaction also appears to be a thermal response occurring only at higher temperatures and governed by the residence time at these temperatures. Sonication, by keeping the temperature low and ignoring the thermal capacity of the mixture in the absence of added water, enables high temperatures to be maintained long enough for browning and also results in a softer caramel.

The second half of the caramel mixture was treated initially as the above sample but on reaching 103°C the reaction was completed thermally by raising the temperature to the 115°C. This results in a very stable caramel. No spread at all is observed at 40°C however an extremely brittle caramel results which 'snaps' very easily indicating water loss as the temperature is raised.

The results obtained indicate that although sonication of caramel in the absence of added water at 103°C leads to a caramel which spreads enormously at 40°C it also manages to retain it's fat content unlike the corresponding thermal caramel. This suggests a better emulsification of the mixture in the presence of sonication. A softer caramel is also obtained via sonication indicating a larger degree of water retention at these temperatures.

Water appears to be necessary for efficient sugar solvation and this reduces the amount of graininess and rigidity of the resultant caramel. Lack of water increases the thermal capacity of the caramel and reduces the residence time at higher temperatures thus limiting the efficiency of the browning reaction. Some water must be therefore be included in the caramel matrix.

8.2.4.2 Alternative Technology using a 5:1 Total Sugar/Total Water Ratio

The effect water has on thermal and sonicated reactions can be shown by reducing the amount of water present from a 3:1 total sugar/total water ratio to a 5:1 ratio.

The thermal preparation of the 5:1 sugar/water ratio caramel was attempted. The resultant caramel indicated only a 4% spread after 24 hours with a high degree of homogenisation of the sample. A similar result was obtained using a 3:1 sugar/water ratio caramel.

Addition of Milk Powder to Sucrose Solution

The order of addition of the constituents was altered. The original addition order involved the addition of milk powder to water and then, after homogenisation the sugar was added. In this experiment sugar was initially added to the water and stirred until it had been dissolved and then milk powder was added to the solution. The mixture produced very hard white powder-like granules on the addition of the milk powder. The granules coagulated and produced problems in stirring and dispersion. The caramel which resulted contained white lumps. The reason for this is that there is not sufficient 'free water' to dissolve and homogenise the milk, too much is involved in solvation of the sugar. The lumps are in fact wetted milk powder surrounding dried milk granules. The resultant caramel indicated an initial 29.5% spread at 40°C but no further spread occurring. This suggests that an alteration in the order of addition of the ingredients for thermal preparation of caramel produces a poor quality product.

The effect sonication has on the product obtained when the normal order of addition of the caramel constituents was changed led to interesting results. Milk powder was added to a sugar solution and the mixture was sonicated for 15 minutes in a small sonic bath. The mixture was stirred every 5 minutes after which time the temperature had reached 85°C. At this point melted fat and glucose syrup were added to this mixture and the temperature dropped to 65°C and heating was resumed in the saucepan until a temperature of 113°C was reached. The resultant caramel exhibited very poor structure retention and after 1 hour 118% spread was observed and 168% observed after 24 hours.

Despite this the product was very smooth. No graininess was observed since the sugar had been completely dissolved by the water in the initial steps of the preparation. On addition of the milk powder and commencement of sonication the milk granules appeared to be disrupted which would encourage the homogenisation of the milk into the caramel matrix. This suggests that sonication may allow the direct introduction of milk powder into the sugar syrup thus avoiding biohazards involved in the movement of milk solution throughout a production plant.

The intensity of power applied to the sugar solution with added milk powder mixture was increased using a sonic horn. This resulted in a smooth caramel which exhibits only 8% spread at 40°C, after 24 hours, indicating that a more effective homogeneous matrix is obtained. The higher power provided applied more efficient solids dispersal and homogenisation.

In the Absence of Added Water

In the following experiments milk powder was added directly to glucose syrup omitting the addition of water. On mixing the milk powder into the glucose syrup a smooth white 'paste' was obtained which readily accommodates the addition of sugar and fat. This mixture was stirred for 15 minutes after which the rest of the constituents were added. Thermally raising the temperature to 113°C and subsequent cooling of the mixture resulted in a caramel with very poor structure retention giving 152.6% spread after 1 hour at 40°C and 225% spread after 24 hours.

Milk powder was added to the glucose syrup in the absence of added water. This mixture was sonicated for 15 minutes in the small sonic bath after which the other constituents were added and the preparation was completed thermally. The resultant caramel exhibited 41.2% spread after 1 hour at 40°C and 83.4% spread after 24 hours. Sonication provided a far higher degree of homogenisation than the corresponding caramel prepared thermally.

Addition of Water and Milk Powder to Glucose Syrup

This experiment was slightly different from that above in that the milk powder was added directly to glucose syrup already containing added water (the previous experiments omitted water).

The thermally prepared caramel involved the addition of water to glucose syrup and subsequent addition of the milk powder. On mixing the milk powder into the glucose syrup and water mixture a smooth white 'paste' was obtained which readily accommodates the addition of sugar and fat. This mixture was stirred for 15 minutes after which the other constituents were added and heated to 113°C. The resultant caramel exhibited 101% spread after 1 hour at 40°C and a further 7% spread after 24 hours.

The corresponding sonicated experiment involved the sonication of the glucose syrup, water and milk powder mixture for 15 minutes in the small sonic bath after which the other constituents were added. The preparation was completed thermally as 113°C was reached. A slightly higher degree of homogenisation was obtained, compared to the previous experiments in the presence of water, with 53% spread obtained after 1 hour at 40°C and 107% after 24 hours.

It appears that under thermal conditions milk powder cannot be efficiently introduced into a solution of sugar but this is overcome (at least partly) by the use of ultrasound. The intensity of the sonication also affects the homogenisation of the sample with much better results at a higher intensity of irradiation.

On mixing the milk powder into the glucose syrup, in the absence of added water, a smooth white 'paste' was obtained which readily accommodated the addition of sugar and fat. This resulted in a higher degree of homogenisation within the resultant caramel for sonicated preparations but thermal preparations revealed very poor structure retention. Addition of water to the glucose syrup and subsequent addition of milk powder increased the degree of structure retention within the thermal preparations by a very large amount but sonicated preparations exhibited a small decrease in structure retention.

These results suggest that thermal preparations require the addition of water for efficient homogenisation but with sonicated preparations water is not as important.

8.2.4.3 Alternative Technology using a 7:1 Total Sugar/Total Water Ratio

A lower water content caramel was investigated with only a 7:1 sugar/water ratio. Water cannot be totally eliminated from the preparation of caramel since it is required for the solubilisation of sugar granules. Insufficient water leads to a grainy textured caramel. To produce a low water content caramel the glucose syrup employed must first be heated to 120°C to reduce its own internal water content. Control thermal preparations were not attempted as these were known to produce grainy products. Several methods employing sonication were attempted.

In the first the constituents necessary for the production of caramel were all added directly to a sonic bath and sonicated for approximately 45 minutes. During this period the temperature was monitored and a maximum of 103°C was reached. The residence time within the sonic bath at the elevated temperatures was sufficient for browning to occur. At this point the sample was halved.

One half of the caramel was cooled directly and exhibited 121% spread at 40°C. The resultant caramel appeared lumpy, indicating inefficient solids dispersal and poor homogenisation. The remainder of the caramel was heated to 113°C. On cooling the resultant caramel exhibited only 27.6% spread at 40°C. A slightly grainy texture was obtained indicating inefficient solubilisation of the sugar within the caramel matrix.

In the presence of higher intensity sonication, applied via a sonic probe at setting 8 (40% output) the maximum temperature of the 500g batch could not be raised above about 73°C. After 25 minutes sonication was discontinued and the caramel batch was again halved.

Half of the caramel mixture was cooled directly. The resultant caramel exhibited 78% spread at 40°C after 1 hour with no further spread observed. A pale caramel was obtained since the temperature was too low for browning to occur. There was inefficient solids dispersal in the sample resulting in a lumpy caramel.

The remainder of the caramel was heated to 113°C. On cooling the resultant caramel exhibited a poor 95.7% spread at 40°C. High power sonication was not effective in this case giving a caramel with poor retention of structure and poor dispersal of solids.

8.2.5 CONCLUSION

The Maillard browning reaction appears to be a predominantly thermal process and the extent of browning is governed by the length of time spent at temperatures of around 100°C.

A grainy caramel texture is obtained on inefficient solvation of sugar into the caramel matrix resulting in the presence of large sugar crystals. Harder and more brittle caramels are obtained as the moisture content of the final product is reduced. This can be reduced either by a decrease in the amount of water added initially or during the preparation of the caramel by heating the sample to overly high temperatures.

It appears that under thermal conditions dry milk powder cannot be efficiently introduced into a solution of sugar but this is overcome by the use of sonication. Mixing milk powder directly into either sucrose solution or glucose solution results in a product with poor structure retention.

In the absence of added water sonicated samples exhibit much higher structure retention than the corresponding thermal samples. In contrast to this on addition of water the thermal samples exhibit a very large increase in the degree of structure retention whereas sonicated preparations exhibit a small decrease. From this one can deduce that thermal preparation is more susceptible to moisture content than preparation involving sonication.

There are several ways in which the application of ultrasound could effect the caramel matrix. One definite benefit of sonication is in the enhancement of the initial emulsification of all the constituents this would improve homogenisation of the fat into glucose syrup or water. The degree of homogenisation would be expected to be greater than the corresponding stirred preparations. This would account for the good texture and structure retention observed in the sonicated samples even in the absence of added water. Reduction of the number of large sugar crystals observed in some sonicated caramel preparations may be due to the mechanical reduction in sugar grain size as well as an increased degree of sugar solubilisation into the matrix.

8.3 EFFECT OF ULTRASOUND ON DISPERSIONS

8.3.1 INTRODUCTION

The initial experimental idea for this exercise was to investigate the possibility that ultrasound might be able to release more cocoa butter from cocoa than conventional technology.

Cocoa grains contain 55% of cocoa butter however in the production of chocolate more cocoa butter must be added. Cocoa butter is a valuable commodity used extensively in foods but also in beauty preparations such as moisturisers. Cocoa butter is removed from cocoa beans by extrusion, this process generally leaves approximately 12% of the butter in the residue which is discarded. This is a considerable waste of a valuable product. It was thought that disruption of the cocoa grain under sonication would occur and thus allow a more efficient extraction of its cocoa butter reducing the overall loss of this material.

8.3.2 EXPERIMENTAL CONDITIONS

The cocoa mixture used for experimentation was prepared as quoted in section 2.10.1.

8.3.3 RESULTS/ DISCUSSION

Effect of Stirring or Sonication on Cocoa Powder

100cm^3 of cocoa was prepared, separated into 25cm^3 volumes and treated in 4 ways.

The first sample was untouched and was employed as a 'control' standard. The second sample was stirred at room temperature for 30 minutes in order to establish the effect of simple stirring on cocoa powder. The third sample was sonicated with a low powered sonic bath for 30 minutes and the fourth sample was sonicated with a higher powered sonic probe for 30 minutes.

The cocoa grains in samples 1,2, and 3 settled to the base of their respective beakers within 30 minutes thus indicating a poor degree of homogenisation and dispersion.

However the fourth sample, which was sonicated with a higher intensity sonic probe, produced a highly homogenised cocoa mixture which did not exhibit any signs of separation even after standing for a period of 1 week at room temperature. This 'homogeneous' cocoa must contain extremely small particulate matter to account for the stability observed.

Solvent Extraction

In order to establish whether cocoa butter was released by sonication the mixtures were treated with solvent to extract and concentrate any liberated butter.

200cm^3 of boiling water was added to 10g of cocoa powder. The solution was then left to cool and separated into 4 samples of 50cm^3 volumes each. 2 cocoa samples were stirred at room temperature for 30 minutes and the remaining 2 were sonicated, with a sonic probe employing the Sonics and Materials equipment at setting 8, for the same length of time.

The individual cocoa samples were extracted with 25cm^3 of solvent, either petroleum ether (40/60) or carbon tetrachloride, in a separating funnel. The samples were shaken for 1 minute and then allowed to separate out.

Petroleum Ether (40/60)

The cocoa mixture was stirred and added to petroleum ether (40/60). Separation of the two layers was slow but eventually the cocoa fell to the aqueous layer and the petroleum ether layer remained clear. This indicated poor disruption of the cocoa powder.

The sonicated sample produced the opposite result. On addition to the petroleum ether a homogenised opaque dark brown solution was obtained which eventually, after days, separated into an opaque petroleum ether layer leaving a clear aqueous layer. This indicates a reduction in grain particle size because the 'settling out' of the cocoa grains to the base of the vessel was prevented. As the cocoa appeared to prefer the petroleum ether layer it can be assumed that the resultant cocoa dispersion is immiscible with water. This may be a result of cocoa butter release, which of course will not mix with the aqueous layer.

The two solutions treated in different ways clearly produced differing cocoa samples.

Carbon Tetrachloride

The cocoa mixture was stirred and extracted with carbon tetrachloride. Separation of the solvents was fast resulting in two distinct layers. The water layer exhibited a dark brown colouration and the carbon tetrachloride a light brown colour suggesting that some part of the cocoa was soluble in carbon tetrachloride. However it is possible that the cocoa sinks into the carbon tetrachloride due to weight rather than simply the extraction of any products.

The sonicated sample was extracted with carbon tetrachloride and a completely homogenised/dispersed solution was obtained with an overall very light brown colour. With time the cocoa slowly sank to the carbon tetrachloride layer with the water layer appearing dark brown (see above).

CENTRIFUGING

In an attempt to isolate any liberated cocoa butter centrifugation was attempted. It was thought that the heavier cocoa material would settle to the base of the vessel and the lighter cocoa butter would float to the surface. In this way the extent of the cocoa butter release would be observed.

50cm^3 of cocoa powder mixture in hot water was placed into an ice bath and sonicated for 30 minutes. This solution was then centrifuged in a small centrifuge for 5 minutes. On inspection a layer of cocoa butter floated to the surface. On removing the dark brown supernatant liquid a layer of solid cocoa granules remained, approximately 30% of the tube volume, and consisted of a smooth, slightly granular, paste. The supernatant liquid was spun in the centrifuge for a further 10 minutes and the resultant liquid was examined yet again. The supernatant liquid appears unchanged, cocoa butter floated on its surface. On further spinning for 15 minutes solid of approximately 1% tube volume settled out of the supernatant liquid leaving the cocoa butter floating on the liquid surface.

Centrifuging was clearly effective in that it removed most of the heavy cocoa grains within the first 5 minutes and that the cocoa butter appeared as a layer on the surface of the liquid. Prolonged spinning increased the amount of cocoa powder removed from the sample.

8.3.4 CONCLUSION

A better homogenisation/dispersion was obtained on sonication of the cocoa mixture resulting in a reluctance of solvent layers to separate. Grain particle size also appeared to be reduced as a less granular textured sample was obtained. Reduction in grain size results in disruption of the individual cocoa grains and release of cocoa butter. Unfortunately cocoa butter could not be separated out of the sample due to the high level of homogenisation/dispersion present.

The amount of cocoa butter released was not determined in this investigation. Further work would be necessary to obtain an accurate quantitative method to differentiate between stirred and sonicated samples. This was not attempted in this study but could be an area for future work.

CHAPTER 9

OVERALL CONCLUSION

9.0 OVERALL CONCLUSION

Ultrasound has been shown to be useful in a wide variety of fields. It is particularly beneficial in solid/liquid heterogeneous reactions where surface erosion or particle size reduction, together with enhanced mass transfer of reagents to the surface increase the rate of reaction considerably. Surface erosion and particle size reduction are two mechanical effects of sonication which are particularly important in processing technology in, for example, the food industry. The photographs obtained from studies of the effect of ultrasound on rice clearly show a large amount of surface damage incurred by the rice grains when sonicated for only a few minutes. Particle size measurements of sugar granules sonicated for 30 minutes in dimethylformamide fell (for icing sugar) from 55μm to 8.3μm and (for granulated sugar) from 1000μm to 29.3μm.

In an extreme case of particle size reduction sonication produced an homogenised cocoa sample from an aqueous suspension of cocoa powder. This homogenised mixture did not separate on standing indicating very efficient grain disruption which could not be achieved via stirring and heating alone.

Particle size reduction is an important factor in many chemical reactions *e.g* size reduction of bases such as potassium carbonate employed in the alkylation reactions of phenols which leads to an overall increase in surface area.

More efficient mass transfer occurs in sonochemical catalysis due to the microstreaming of materials to and from the catalyst surface. This and the pitting of the catalyst surface by microjets, formed in the solvent, all combine to provide an increased rate of reaction in the presence of sonication above that observed under conventional thermal conditions. In these cases the best results are obtained using solvents with high boiling points and low vapour pressures.

An example of sonochemically assisted catalysis is the sonochemical dehydrogenation of tetrahydronaphthalene employing a palladium/ carbon catalyst. The sonicated reaction was shown to occur 20-40°C below the corresponding thermal reaction. With the thermal reaction the most efficient dehydrogenation was achieved in a high boiling ethereal solvent, *e.g.* diethylene glycol dimethyl ether, whereas the sonicated reaction was favoured by high boiling hydroxyl solvents, *e.g.* diethylene glycol.

Ultrasound has also been shown to affect reactions in a manner different from that expected using conventional methodology. For example a reaction occurring under normal conditions would be expected to respond to an increase in temperature with an increase in rate of reaction. Sonicated reactions however are best performed at lower temperatures where the lower vapour pressure produces more effective cavitation.

Studies involving the alkylation of 2,6-dimethylphenol have revealed other factors which have to be considered when attempting sonochemical reactions including reaction volume, reagent concentration and sonication power. However care must be taken when increasing power since power may cause decoupling of the vibrating source with the liquid medium, as shown in dosimetry measurements. This reduces the efficiency of cavitation and is the reason why an 'optimum' power for sonication is often quoted in the literature.

The products from the alkylation of 5-hydroxychromone-2-carboxylic acid ethyl ester derive from O-alkylation, transesterification (or both). The product distribution was found to depend upon the reaction technique employed, *i.e.* it was found possible to control the end product distribution by selecting the appropriate reaction conditions and the appropriate phase transfer catalyst. Thus alkylation with 2-bromobutane produced the

O-alkylated product when employing thermal or sonicated reaction conditions. When employing phase transfer catalysis however a transesterified product could be obtained with Aliquat 336 but an O-alkylated product was formed using a crown ether.

For the heterogeneous reactions studied, sonication provided a more effective means of improving the rate than heating. Further work could be undertaken to examine the enhancement of other dehydrogenation and heterogeneous catalytic reactions.

With the increasing use of sonochemistry as a synthetic technique it is important that the 'energy' of sonication should be monitored. Three calibration methods, *i.e.*calorimetry and the potassium iodide and the ferric ion dosimeters, were investigated and all produced similar trends with respect to equipment and reaction vessel type. Addition of carbon tetrachloride increased the sensitivity of the potassium iodide dosimeter although its reproducibility was reduced. For this system it was essential to ensure complete emulsification of carbon tetrachloride in the medium.

The ferric ion dosimeter, an homogeneous system, did not require emulsification. However this method was less sensitive than the potassium iodide/ carbon tetrachloride dosimeter, due mainly to the low ultraviolet/ visible absorption of the ferric ion.

Finally calorimetry was shown to be a convenient method of determining the efficiency of sonication since power applied can be directly measured as the temperature rise within the reaction medium.

The application of sonication to the processing of food is a relatively new field with possible applications including such factors as emulsification, crystallisation, particle size reduction and filtration of the food materials.

Studies involving the reduction in viscosity of starch solutions revealed that cornstarch was not affected by sonication. However a reduction in viscosity was observed for the individual components of starch with amylopectin achieving a permanent and amylose a temporary viscosity reduction during irradiation. This area of study is complex and suggests that more efficient measurements of viscosity should be undertaken together with an examination of the polydispersity of starch samples (*e.g.* gel permeation chromatography). Both investigations could provide interesting results.

The amount of cocoa butter released from cocoa grains on sonication was not quantified. Further work will be necessary to determine the efficiency of cocoa butter extraction. Efficient homogenisation of cocoa was obtained on sonication of a sample, suggesting efficient grain disruption and cocoa butter release. Extraction of cocoa is very important within the food and cosmetic industries and if a more efficient method of extraction could be developed it would be quite an exciting achievement.

There can be no doubt from the work completed in this thesis and the ever increasing volume of literature on the subject that sonochemistry is a broadly based and expanding field of research. Undoubtedly the subject has gone beyond the laboratory stage and many groups are now engaged in scale-up. We believe that our studies have demonstrated that power ultrasound is a usable tool in both chemical synthesis and the processing industries on a small and intermediate scale with real potential for industrial usage.

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10.0 REFERENCES

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