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**THE EFFECT OF FREQUENCY ON
SONOCHEMICAL REACTIONS**

BY

MOHAMMAD H. ENTEZARI, M.Sc.

THESIS

**Submitted in partial fulfilment
of the requirements for the degree
of Doctor of Philosophy in Chemistry of the
Faculty of Graduate Studies and Research**

Chemistry Department

Carleton University

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THE EFFECT OF FREQUENCY ON SONOCHEMICAL REACTIONS

ABSTRACT

Ultrasonic irradiation, or sonication, is a unique method of activating and accelerating chemical reactions in a liquid medium through the action of cavitation. Typically, ultrasonic irradiation can increase the rates of reactions, decrease the required reaction temperature and improve product yields.

Historically, the effect of frequency on sonochemical reactions has been considered to be negligible. It was thought that when the ultrasonic power is sufficient to produce cavitation, it does not matter what frequency is used. We focussed our study on the effect of frequency on different sonochemical reactions in order to test this assumption.

The frequencies generally used in sonochemistry are in the range of 20-100 kHz. Only a very few groups have used ultrasound with frequencies outside this range. Since cavitation is responsible for sonochemical effects, there is however no reason to restrict our studies to this normal frequency range. Our work focussed on two different frequencies far from each other, 20 and 900 kHz. The 900 kHz apparatus was specially designed and constructed; using a commercially available power supply.

The effects of temperature, intensity, and gas were investigated at these two different frequencies. It was found that the behaviour with 900 kHz irradiation can be very different from that with 20 kHz. For example, the sonication of potassium iodide solution under the same conditions was more

effective with 900 kHz than 20 kHz. Sonication of chlorobenzene in water with 900 kHz led to a yellow solution with a high rate while with 20 kHz this reaction was very slow. However, the sonication of liquid carbon disulfide with 20 kHz led to a heterogeneous system, while sonication with 900 kHz had no apparent effect. Our results suggest that the surface area of the sonicator is very important.

There seems to be a dependence of the reaction rate on irradiation frequency arising from the temporal and spatial characteristics of the cavitation bubbles produced. The bubble size and collapse time are significantly different at the two frequencies. This may have an important role in determining the different behaviours observed. A sonochemical reaction can occur in the gas phase inside the bubble, at the interface, or at some distance away from cavitating gas bubble. This may be another important consideration in explaining the difference in results with frequency.

**This thesis is dedicated to my late father,
my mother, my wife Foozleh Farzin and
my lovely daughter Kimia who came
on the right time (Nov. 3, 1994).**

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CHAPTER 1

INTRODUCTION TO SONOCHEMISTRY

1.1 Introduction

Ultrasound is best known through its industrial and medical applications. The term refers to acoustic waves with a frequency above 16 kHz, the limit for human hearing. In industry, it is used for applications such as welding plastics, dispersing pigments in paint and cleaning and degreasing of articles by immersion in ultrasonic baths. In medicine, high frequency ultrasound (2-10 MHz) is used for sonographic imaging of fetuses, non-surgical removal of kidney stones and also in physiotherapy. Ultrasound is also used in tumor treatment. The sonodynamic therapy is a use of sonochemical activation of special agents by ultrasound irradiation focused into the tumor [Umemura, 1992]. Lower frequencies (20-50 kHz) are used in the treatment of muscle strains.

Sonochemistry is the study of the interaction between the ultrasonic waves and liquids. These can be homogenous solutions or heterogeneous slurries [Rooney, 1988; Rooney, 1981; Rudenko, 1977]. This interaction is unique and quite different from the interaction of other energy sources such as light, heat or ionizing radiation, as shown in Figure 1.1 [Suslick, 1989]. The interaction can have physical effects, such as erosion and emulsification, as well as chemical effects, such as production of radicals and other excited species. These effects result from acoustic cavitation and microstreaming. The latter effect constitutes an unusual fluid flow associated with velocity gradients and streaming stresses [Rooney, 1988].

Figure 1.1: A comparison of different energy sources of chemical reactions (Suslick, 1989).

From a historical point of view, the first chemists who discovered the unusual effects of intense ultrasonic waves in liquids, known as sonochemistry, were Richards and Loomis in 1927 [Richards, 1927]. They described two types of conventional chemical reactions in aqueous solutions which were accelerated by ultrasound. In 1935 Frenkel and Schulze reported for the first time that water emits light when exposed to intense ultrasound. They proposed that the sudden cavitation in water is accompanied by charge separation; an electrical discharge should then occur in a bubble. Brohult [1937] was the first to describe the degradation of a biological polymer in 1937. Schmid [1940] carried out the first experiments with synthetic polymers. A number of other researchers such as Boyce, Harvey and Kornfeld and Suvorov [1944] investigated various aspects of ultrasonics in the 1930s and 1940s.

There was no significant progress in sonochemistry until the 1980s, when a renaissance took place in this field. This renaissance was due to the advent of inexpensive and reliable generators of high-intensity ultrasound.

1.2 Cavitation:

The term "cavitation" was first used by Sir John Thornycroft and Sydney W. Barnaby in their observation of propeller inefficiency in torpedo boat destroyers [Thornycroft, 1895]. Lord Rayleigh [1917] studied this mechanical cavitation problem in 1917 and confirmed that the vibrations were due to the enormous turbulence, heat, and pressure of imploding cavities.

Cavitation is now the name used to describe the formation and the subsequent dynamic life of bubbles (cavities) in liquids. These cavities may be filled with gas and/or vapour, and they can be produced in a wide variety of liquids under different conditions. Cavitation can occur in fluids such as water, organic solvents, biological fluids, and molten metals.

The origin of cavitation can be hydrodynamic, acoustic, thermal, or some other effect. Scientists are still seeking ways to prevent the occurrence of hydrodynamic cavitation in various installations such as pumps and valves. Cavities can have a significant effect on liquid-flow rates through pipes. More importantly, the collapse of the cavities may produce intense shock waves which can cause considerable damage to surrounding material. A good example of this provided by ships' propellers, where the collapse of the cavities produced by the mechanical churning of the blades causes a considerable erosion of the blades. In this present work, acoustic waves as the origin of cavitation will be focused on in more detail.

1.3 Acoustic cavitation

The chemical effects of ultrasound do not arise from a direct coupling of the acoustic field with the molecular species. This is because the acoustic wavelength in liquids is from 10 to 10^4 cm, with associated ultrasonic frequencies of from about 15 kHz to 1 GHz. Instead, chemical effects come from the most important nonlinear acoustic process, cavitation. Acoustic

cavitation can be divided into three discrete stages : formation, growth and implosive collapse [Suslick, 1989, 1990; Flynn, 1964; Apfel, 1981; Mason, 1990]. Figure 1.2 shows an idealized representation of these stage in cavitation process [Suslick, 1989].

The propagation of acoustic (i.e. ultrasonic) waves in a liquid medium is accompanied by compression and expansion cycles. Compression cycles exert a positive pressure on the liquid in addition to the mean pressure in the medium, which pushes the molecules together. Inversely, expansion cycles exert a negative pressure on the liquid which moves molecules further apart. The negative pressure exerted by expansion cycles on the liquid must exceed the attractive forces between molecules, or the liquid 's tensile strength, in order to form cavities.

In theory, a negative pressure of more than 1000 atmosphere is required to cause cavitation in pure water [Crum, 1982]. Experimentally, however, we know that cavities can be formed in a liquid with a negative pressure of only a few atmospheres. The difference between theory and experiment can be explained by the presence of heterogeneous impurities, gas bubbles or solid particles, which constitute points of weakness of the liquid structure. In other words, the cohesive forces are disorganized by contaminants which can be found even in ultrapure liquids. It is generally accepted that the nucleation mechanism involves gas trapped in small crevices of hydrophobic contaminants. During the rarefaction cycle (negative pressure cycle), the liquid-gas interface

Figure 1.2: *An idealized representation of the acoustic cavitation process which includes formation, growth and implosion (Suslick, 1989).*

becomes increasingly convex. At a sufficiently negative acoustic pressure, this gas is released [Crum, 1979; Winterton, 1977; Apfel, 1970], producing smaller free bubbles in the solution. It can also itself collapse violently [Crum, 1982a; 1982b].

Once a bubble is formed, three things can happen, depending on the size of the bubble. If the bubble is large, it will float away and burst at a surface; if it is very small, it will redissolve into the liquid. A bubble in a special range of size can however interact with an ultrasonic wave so that it absorbs energy from alternating cycles of the wave. Under some conditions the ultrasonic wave can continue to cause the bubble to oscillate around an equilibrium size. In some cases, however, the average size of the bubble increases.

The mechanism of cavity growth is termed "rectified diffusion"; it is important at low acoustic pressures [Flynn, 1992]. In the negative phase of the acoustic wave, gas diffuses from the liquid into the bubble, while in the positive phase, the diffusion of the gas is reversed. This process has been modelled mathematically [Strasberg, 1959; Safar, 1968; Gould, 1974; Eller, 1975; Crum, 1982c]. Since the interfacial area is greater in the negative phase than positive phase, the process leads to an overall growth of the bubble. The cavity will grow slowly over many cycles and eventually reach a resonant or critical size, where it absorbs a maximum of energy from the ultrasonic wave (see Figure 1.2). In this situation the cavity can grow rapidly and can no longer

absorb energy efficiently from the ultrasonic wave. Under this condition the cavity can not sustain itself any longer, the liquid rushes in, and the cavity implodes. This implosion resembles adiabatic compression and creates a local "hot spot" which establishes an unusual environment for chemical reaction.

Flynn [1992] has proposed two extreme types of cavitation: stable and transient cavitation. For stable cavitation the time is sufficiently long for mass diffusion of gas, as well as thermal diffusion. If the rates of mass transfer across the gas-liquid interface are not equal, bubble growth may result. In transient cavitation, a short-lived bubble undergoes dramatic volume changes in a few acoustic cycles and terminates in a violent collapse. During the lifetime of the transient bubble, it is assumed that there is not enough time for mass transfer by diffusion of gas into or out of the bubble, whereas evaporation and condensation of liquid is assumed to take place freely. Both stable and transient cavitation may occur simultaneously in a solution, and a bubble undergoing stable cavitation may become a transient cavity [Flynn, 1992].

1.3.1 Factors affecting acoustic cavitation

As sonochemistry is derived from acoustic cavitation, the parameters which affect the cavitation process most certainly will alter the sonochemical reactions. The most important factors which have a significant influence on the cavitation process are: presence of gas, liquid properties, bulk temperature, and acoustic characteristics.

1.3.1.1 Gas

The removal of gas from a liquid reduces the available nuclei and it becomes more difficult to cavitate that liquid. In addition, several properties of the gas or vapour in the bulk have dramatic effects on the cavitation collapse [Prudhomme, 1957; Yong, 1976; Suslick, 1990]. The ratio of heat capacities $\gamma = (C_p/C_v)$, is one of the important physical parameters that affects sonochemical reactions. By assuming that the gas inside the bubble behaves as an ideal gas and that the collapse is an adiabatic process, the effect of γ on the collapse of bubbles can be modelled, as shown below:

$$p_i V_i^\gamma = p_f V_f^\gamma \quad [1-1]$$

$$T_f = \frac{T_i}{\left(\frac{V_f}{V_i}\right)^{\gamma-1}} \quad [1-2]$$

Here p_i , V_i , T_i , p_f , V_f and T_f are respectively the initial and final pressures, volumes and temperatures of the bubble. According to the above equation, with increasing γ , the final temperature also increases. Using gases with large γ values will thus provide larger sonochemical effects. Due to this reason, monatomic gases such as He, Ar and Ne are used in preference to diatomic and polyatomic gases.

Since γ for Ar, He and Ne are equivalent, their collapse should generate the same heating, if the collapse were fully adiabatic. These gases have however different solubilities in liquids. In addition, the collapse is also affected by the thermal conductivity of the gas as it is assumed to be adiabatic. Thus, gases with the same γ affect sonochemical reactivity differently owing to differences in solubility and thermal conductivity. For illustration, Table 1.1 shows the rate of formation of free chlorine by irradiation of water containing CCl_4 in relation to the nature of the saturating gas [Yong, 1976].

A gas with higher thermal conductivity allows more energy to dissipate into the surrounding medium during collapse, reducing the adiabaticity of the collapse. Therefore, the maximum sonochemical reactivity is observed in cases of a gas with high γ and low thermal conductivity. It is assumed that the gases do not participate directly in primary or secondary chemical reactions caused by the ultrasound.

Table 1.1: Rate of formation of free chlorine by sonication of water containing CCl_4 under different saturating gases

Type of Gas	Reaction Rate (mM/min)	Heat Capacity Ratio (γ)	Thermal Conductivity ($10^{-2}\text{W m}^{-1}\text{K}^{-1}$)
Ar	0.074	1.66	1.73
Ne	0.058	1.66	4.72
He	0.049	1.66	14.30
O_2	0.047	1.39	1.64
N_2	0.045	1.40	2.52
CO_2	0.028	1.43	2.72

1.3.1.2 Liquid properties

In sonication of a liquid, the bubbles contain not only gas but also vapour. Liquids with high vapour pressures undergo less intense cavitation effects. This is most easily demonstrated by the maximum temperature produced on implosion. Since liquid molecules in the vapour phase inside a bubble usually have a low heat capacity ratio (less than 1.2), there is a decrease in the maximum cavitation temperature attainable by the collapse of cavity. Due to compressibility of the solvent vapour, the adiabaticity of the collapse is reduced [Fujikawa, 1980]. The bubbles containing vapour molecules can also undergo chemical reactions which remove energy from the bubble, thus decreasing even more the final temperature attainable during collapse of cavity [Fogler, 1969].

Surface tension is the other property of liquids that can have an effect on the cavitation process. Liquids with low surface tensions should have a low cavitation threshold. However, Crum [1982d] observed an increase in cavitation threshold with a decrease in surface tension of distilled water by hydrophobic solids.

The viscosity of a liquid also influences the cavitation process. The formation of a cavity is more difficult in highly viscous liquids. This can be explained by the quantity of negative pressure in the rarefaction region which is required to overcome the cohesive forces acting within the liquid (see Table 1.2).

Table 1.2: Acoustic pressure (p) producing cavitation in various liquid under atmospheric pressure [Bergmann, 1938].

Liquid	Viscosity N s m ⁻² (25°C)	Pressure (atm)
Castor oil	0.630	3.90
Olive oil	0.084	3.61
Corn oil	0.063	3.05
Linseed oil	0.038	2.36
CCl ₄	0.001	1.75

1.3.1.3 Bulk temperature

Temperature variations affect the cavitation process through gas solubility, surface tension, and vapour pressure. For example, as the bulk temperature is raised, the vapour pressure of the liquid increases. The greater vapour content inside the cavities causes more cushioning action during the compression, weakens the collapse, and reduces the cavitation intensity. Thus, any effect directly related to cavitation should correspondingly decrease with an increasing temperature.

The results on the chemical and physical activity of cavitation as a function of liquid temperature can be divided into three categories: those that are initially independent of temperature changes and then decrease rapidly [Weissler, 1953; Lindstrom, 1955]; those that decrease exponentially [Rosenberg, 1960; Sehgal 1980]; and finally, those that increase initially and after an optimum temperature decrease [Ibisi, 1967]. These different types of

behaviour might be due to the phase in which the reactions occur. The reaction zones can be in the liquid medium, in the gaseous phase within a cavity, or at a liquid-gas interface.

1.3.1.4 Acoustic characteristics

Acoustic intensity has a dramatic effect on the rates of sonochemical reaction. At very low intensities below the threshold for cavitation, the amplitude of the sound field is not enough to induce nucleation or bubble growth. Above this threshold the reaction rate increases with ultrasonic intensity. However, several investigators have noted that there is an optimum intensity for formation of cavitation bubbles, above which further increases cause a decrease in yield [Nomoto, 1948; Bondy, 1936]. This behaviour at high intensities can be due to growth of very large bubbles which float away from solution, as well as a diminishing of the penetration of the ultrasound into the liquid due to production many bubbles near the radiating surface.

In the literature, the effect of ultrasound frequency has been considered as a negligible or secondary effect on the nature of most sonochemistry. In acoustic cavitation, most experiments have been carried out by means of frequencies in the range of 20-100 kHz. There are some works with high frequency [Henglein, 1992, 1990, 1984; Hart, 1985; Fischer, 1986; Petrier, 1992]. However, as will be shown in this thesis, sonochemistry at higher frequencies (MHz) shows interesting aspects which differ from those at low

frequencies.

Since the cavitation process is responsible for sonochemical effects, there is in principle no reason for restricting the sonochemical reactions to a frequency range between 20 kHz and a few MHz. It seems that any sound frequency which causes cavitation process can be studied regardless of its frequency. Lower frequencies have traditionally been used since equipment for its generation is more developed. Cavitation thresholds are also lower at lower frequencies.

1.4 Acoustic cavitation and chemical reactions

Over the past few years a large number of chemists (physical and synthetic) and engineers have worked extensively on sonochemical reactions, including a wide range of homogeneous and heterogeneous reactions and material processing.

In chemical synthesis, ultrasound has many uses, and several reviews of its applications to organic synthesis have been seen in the literature [Suslick, 1988; Einhorn, 1989; Mason, 1990]. In the field of polymers, power ultrasound has been used primarily for the depolymerization effect of ultrasound [Price, 1990]. However, in a series of papers Peeter Kruus and co-workers [1983, 1985, 1987, 1988] showed that polymers such as polystyrene and poly(methyl methacrylate) could be produced simply by sonication of pure, dry monomers. Both polymerization and depolymerization by ultrasound could be a useful

method for controlling polymer structure as well as improving the rates and yields of many common polymerization reactions [Price, 1993]. High intensity (power) ultrasound has also been used in metallurgy to improve the gas release from melts and the grain refinement of metals.

Power ultrasound influences the system through the generation and destruction of cavitation bubbles. In order to understand the mechanism through which cavitation collapse can affect chemical processes, one must consider this effect in different systems. These chemical effects of ultrasound fall into two major categories: homogeneous sonochemistry of liquids and heterogeneous sonochemistry of liquid-solid or liquid-liquid systems.

1.4.1 Acoustic cavitation and homogeneous reactions

The collapse of a bubble during sonication in a homogeneous liquid is spherically symmetric. Lauterborn studied the laser induced spherical cavitation of single bubbles in water far from boundaries [Lauterborn, 1973]. He was able to photograph the collapse of a single spherical bubble at a speed of 75,000 frames per second (see Figure 1.3). Lauterborn [1980] also repeatedly took photographs of the collapse of a single spherical bubble at a million frames per second. Even at this high speed they could not fully resolve the final collapse, but the radiation of a shock wave was clearly demonstrated.

The bubble contains vapour from the solvent and any volatile reagents subjected to the enormous increases in both temperature ($\approx 5000^{\circ}\text{C}$) and

Figure 1.3: *Laser-induced spherical cavitation bubble in water far from boundaries (Lauterborn, 1973).*

pressure (≈ 500 atm) in the collapse process. These extreme conditions produced by imploding bubbles last for less than a microsecond [Suslick, 1986], causing molecules to fragment and generating highly reactive radicals species. These radicals may either react within the collapsing bubble or migrate into the bulk liquid.

Suslick et al. [1986] determined the effective temperature reached during cavitational collapse by the use of competing unimolecular reactions for which the dependence of the rates on temperature is known. The sonochemical ligand substitutions of volatile metal carbonyls were used as the comparative rate probes. These studies revealed that there were two sonochemical reaction zones. One reaction zone occurred in the bubble's gas phase and the second one took place in an initial liquid zone surrounding the bubble. The effective temperature of these zones was estimated at 5200 ± 650 K in the gas phase zone and about 2000 K for a zone about 200 nm from the bubble surface [Suslick, 1986].

Ultrasonic irradiation of water [Weissler, 1959; Lippit, 1972] was one of the first homogeneous sonochemical reactions studied. In the primary reaction, water itself decomposes with the formation of radical species ($\text{OH}^\bullet$ and $\text{H}^\bullet$). Any component dissolved in the water will be subjected to chemical reaction with these ultrasonically produced radicals. Riesz and co-workers [1985] were able to detect these highly reactive radicals by using spin traps.

The presence of iodide in aqueous solution under sonication will release

iodine molecules owing to the reaction between iodide and hydroxyl radical. Some other examples of homogeneous sonochemical reactions are: chlorine formation from carbon tetrachloride [Weissler, 1950], ammonia synthesis [Sokol'skaya, 1957], oxidation of aldehydes [Vasilina, 1984], metal carbonyl substitution [Suslick, 1984], and iron oxidation [Price, 1993].

1.4.2 Acoustic cavitation and heterogeneous reactions

The bubble collapse in a heterogeneous system is completely different from that in a homogeneous one. Figure 1.4 [Lauterborn, 1975] shows a collapse of a single spherical bubble produced by laser near a plane solid boundary in water. The framing rate is 75000 frames per second. As observed in Figure 1.4, a microjet is formed in an asymmetric collapse of bubble. This jet has a velocity of roughly 100 to 200 m/s as determined by the high-speed microcinematography [Lauterborn, 1975].

1.4.2.1 Physical point of view

The implosion of a cavity on the surface causes severe substrate damage. It has been suggested that high velocity jets forming during bubble collapse are responsible for surface damage due to their impingement on the surface [Nyborg, 1978; Tomita, 1986]. Shockwaves created by collapse of cavities in the liquid also induce surface damage. These two mechanisms (microjet and shockwave) are thought to be responsible for localized erosion

Figure 1.4: *Collapse of a single, spherical, laser-induced cavitation bubble near a solid boundary (Lauterborn, 1975).*

and also the sonochemical effects on heterogeneous reactions.

Ultrasonic cleaning is a technique which is used commonly for particle removal. This technique has been successful in the removing some particular contamination from hard substrates [Kashkoush, 1990, 1992]. Surface contamination by submicron-size particles is a major problem in the semiconductor industry. As the line width in the circuits decreases to less than a micron, the problem of contamination control becomes more serious.

The main mechanisms responsible for the cleaning process in an ultrasonic field are cavitation, acoustic streaming and the formation of a pressure gradient across the particles [Kashkoush 1990, 1992; Geers, 1991]. The removal of contamination was studied by high speed photography [Rozenberg, 1960]. He determined two independent mechanisms for removal of contamination films. The first one was the partial tearing of a film from the surface by the collapse of the bubble; the second was the penetration of energetic small bubbles into all pores and gaps between the contamination layer and surface. The vibration of this bubbles facilitated the peeling, tearing off pieces of the contamination layer from the surface.

A simple model for removing a micron size spherical particle adhering to the smooth solid surface was proposed by Geers [1991]. Also Olson [1988] studied the interaction between a plane acoustic wave and a spherical particle. Both of them claimed that the pressure was the driving force responsible for particle removal from flat surfaces.

1.4.2.2 Chemical point of view

Reactions involving solids in liquid can be divided into two groups: one in which the solid is consumed as a reagent; the other in which it acts as a catalyst in the process.

Historically, Renaud [1950] was the first to use ultrasound in heterogeneous liquid-solid reactions. He prepared some organometallic compounds with metals such as Al, Li, Mg.

In the case of metal powders, there is considerable surface change and reduction in particle size. This is due to cavitation collapse on or near the surface. These effects may lead to an increased reactivity of solid reagents by: (a) removal of passivating surface coatings such as oxides; (b) reduction of particle size, which presents a much greater surface area to the liquid resulting in an enhanced rate; (c) improvements in mass transport; (d) creation of surface defects which may lead to reactive centres in some cases.

Suslick and coworkers have studied the effect of ultrasound on some metals such as zinc, nickel and copper [Suslick, 1987, 1989a, 1989b]. As a result of the effects caused by sonication, these metals have greatly increased effectiveness as catalysts [Suslick, 1986]. For example, the hydrogenation of alkene by Ni powders is enormously enhanced (by about 10^5 times) by ultrasound irradiation [Suslick, 1987]. In these studies Suslick and coworkers observed a dramatic changes in morphology; they also confirmed that the ultrasonic irradiation effectively removed the surface oxide coating by studying

the surface composition using an Auger electron spectroscopy.

Ultrasonic irradiation of slurries causes an acceleration of the movement of particles. These particles can collide head-on or at glancing angles and owing to high speed, the interparticle collisions can produce temperatures above the melting point. The particles can finally fuse to each others. A scanning electron micrograph of two zinc particles with average diameter of about 10 μm after interparticle collision by ultrasound is shown in Figure 1.5 [Doktycz, 1990]. This micrograph also shows a neck region formed in the impact area.

Ultrasound can promote heterogeneous reactions, even those which normally are quite ineffective under normal conditions. Ando [1984], Boudjouk [1983], Luche [1980], and Suslick [1984] among others have done some work in this area. The following reactions show a few simple examples of their work.

Figure 1.5: *Scanning electron micrograph of two Zn particles which produces a neck from localized melting caused by sonication (Doktycz, 1990).*

The molecular intercalation in a heterogeneous system is a difficult reaction which is facilitated by high intensity ultrasound [Chatakondur, 1987]. The intercalation of organic or inorganic compounds (guest molecules) between the atomic layers of inorganic solid (hosts molecule) produces a dramatic changes in catalytic and electronic properties of host compounds. These reactions usually are very slow and require high temperatures and long times for completion; ultrasound can increase the rate by a factor of 200.

In the case of liquid-liquid heterogeneous systems, sonication provides rapid and efficient emulsification of any immiscible liquids, resulting in a large surface contact area for reaction.

1.5 Theories of cavitation

There are several theories and models for describing ultrasonic cavitation. Owing to complicating factors involved in the cavitation process, it is difficult to find a single theory or a model which is capable of giving an answer for every situation. In most sonochemical experiments there is a multitude of cavitation bubbles which can behave in different ways. Generally, it is possible to divide these theories and models into two major groups: electric discharge and thermal theories.

1.5.1 Electric discharge theory

In 1935 Frenkel and Schulze reported for the first time the emission of

light from water sonicated by intense ultrasound. They proposed that the cavitation process in water is accompanied by charge separation, similar to the charge separation that occurs in the atmosphere. The discharge theory of Frenkel [1940] involves the formation of a lens-shaped cavity with the two sides of the cavity oppositely charged. When the cavity continues to grow, the magnitude of the charge on each side of the cavity increases, and the electrical field within the cavity increases until a discharge across the cavity occurs. Such a discharge is assumed to be accompanied by a flash of light, ionization and chemical reactions.

This model remained a significant influence for a long time so that it was believed to be the major cause of sonochemical effects [El 'piner, 1964]. This was one reason why only a few sonochemical investigations were done on organic liquids. Such liquids have low dielectric constants and were predicted by the theory to be sonochemically unreactive.

Margulis [1991] has proposed a new electrical theory of cavitation phenomena. He claimed recently [1994] that the "hot spot" theory can not explain many experimental results, such as the dependency of the sonochemical rate on temperature near the boiling point, on hydrostatic pressure near the saturated vapour pressure of the liquid, and on high viscosity. He concludes that his new electrical theory provides a good alternative to the "hot spot" theory.

1.5.2 Thermal theory

Rayleigh [1917] first described theoretically the collapse of a spherical cavity. The first systematic study of acoustic cavitation was carried out by Blake [1949], followed by Noltingk and Neppiras [1951]. This model did not involve electric effects. It focused on describing the size, temperature and pressure of the bubbles in an acoustic field. There is a useful review of such models of cavitation in Flynn 's paper [1964]. More recent reviews are available in a series of papers in Ultrasonics [Neppiras, 1980; Prosperetti, 1984; Apfel, 1984].

1.5.2.1 Bubble dynamic equation

The following equation is known as the Rayleigh-Plesset equation, developed by Plesset [1949]. It governs the motion of the bubble in the applied acoustic field in liquid.

$$R\ddot{R} + \frac{3}{2}\dot{R}^2 = \frac{1}{\rho} [p_L - p_\infty(t)] \quad [1-3]$$

Here, R is the instantaneous bubble radius, $\dot{R}$ the velocity of the bubble wall, $\ddot{R}$ the bubble wall acceleration, p_L the pressure at the bubble-liquid interface, $p_\infty(t)$ the pressure due to the acoustic field, and ρ the liquid density.

A bubble with radius R at equilibrium in a liquid has on it the pressure of

the bubble walls arising from the hydrostatic pressure (p_L) within the liquid and the surface tension (σ). For equilibrium, this must equal the internal pressure (p_i) responsible for attempting to expand the bubble; p_i has contribution from the trapped gas (p_g) and vapour (p_v) of the liquid. This explanation is shown in the following equation:

$$p_L = p_i - \frac{2\sigma}{R} = p_g + p_v - \frac{2\sigma}{R} \quad [1-4]$$

The gas pressure inside the bubble is changed when there is a change in the radius. When it is assumed that the gas is ideal and that the total amount of gas in the bubble remains constant, then the bubble radius and the gas pressure are related by

$$p_g = p_{g0} \left(\frac{R_0}{R} \right)^{3\alpha} \quad [1-5]$$

Here, p_{g0} , R_0 are the initial pressure and radius and p_g , R are the final ones respectively. The value of α is unity for an isothermal process, while it is equal to the heat capacity ratio (γ) for an adiabatic process.

The acoustic pressure (p_a), the time-varying pressure field, is obtained from the characteristics of the ultrasonic radiation. If it is a sinusoidal function

of time, then it can be written as

$$p_{\infty}(t) = p_0 - p_A \sin \omega t \quad [1-6]$$

which p_0 , p_A and ω are ambient pressure, maximum pressure amplitude and angular frequency, respectively. Substituting equations [1-4], [1-5], and [1-6] into equation [1-3] and rearranging, we obtain

$$\ddot{R} = \frac{1}{\rho} \left[p_{g0} \left(\frac{R_0^{3\kappa}}{R^{3\kappa+1}} \right) + \frac{p_v}{R} - \frac{2\sigma}{R^2} - \frac{(p_0 - p_A \sin \omega t)}{R} \right] - \frac{3\dot{R}^2}{2R} \quad [1-7]$$

This equation describes the radial motion of an isolated gas-filled bubble in an incompressible liquid with specific physical characteristics (ρ , σ , γ , p_v) under an acoustic pressure. Figure (1.6) shows a set of solutions of equation [1-7] for increasing values of the ratio p_A/p_0 [Akulichev, 1967]. At low intensities the motion is stable, but it becomes transient at a certain threshold p_A . When p_A exceeds this threshold, the bubble grows too large and can collapse completely during the first acoustic cycle. At higher intensities the collapse may happen during the second, the third or subsequent cycles. Eventually, a point is reached where the bubble grows so large that it can never collapse as a transient (upper threshold).

Figure 1.6: Radius-time curves for pulsations of air bubbles in water (the numbers on the curves refer to p_A/p_0). $R_0 = 5 \times 10^{-4}$ cm; $\omega = 4.2 \times 10^6$ s $^{-1}$; $p_0 = 1$ bar.

More exact models which are more complicated and difficult to handle have also been derived. These take account of viscosity, thermal exchanges, and liquid compressibility to various extents [Flynn, 1964; Akulichev, 1971; Neppiras, 1980]. However, equation [1-7] is realistic for all ordinary stable cavitation conditions, in the threshold region, and also for transient cavitation up to the point where the collapse velocity approaches the velocity of sound.

1.5.2.2 Lifetime of bubble collapse

Rayleigh [1917] deduced the cavity collapse time (τ) by considering the total collapse of an empty void (radius of R_m to zero) under the action of a constant pressure (p_0). The collapse time is given as

$$\tau = 0.915 R_m \left(\frac{\rho}{p_0} \right)^{\frac{1}{2}} \quad [1-8]$$

where R_m is the radius of the cavity at the start of collapse. This equation [1-8] can be modified for a bubble being filled with either gas or vapour, giving

$$\tau = 0.915 R_m \left(\frac{\rho}{p_m} \right)^{\frac{1}{2}} \left(1 + \frac{p_{vg}}{p_m} \right) \quad [1-9]$$

Here, p_m is the sum of atmospheric (p_0) and acoustic pressure (p_a), and p_{vg} is the pressure inside the bubble (vapour and gas).

The range of the collapse lifetimes is estimated to be from 5 ns to 5 ms [Margulis, 1991, 1985, 1982; Benkovskii, 1974]. A collapse lifetime less than 100 ps has, however, been reported by Barber and Putterman [1991]. They determined the lifetime by monitoring the sonoluminescence from a single bubble in a 20 kHz acoustic field.

1.5.2.3 Temperature and pressure in a collapse cavity

The maximum temperature and pressure at the collapse of the bubble can be derived from the bubble dynamic equation.

$$p_{\max} = p_g \left[\frac{p_m(\gamma-1)}{p_g} \right]^{\frac{\gamma}{\gamma-1}} \quad [1-10]$$

$$T_{\max} = T_0 \left[\frac{p_m(\gamma-1)}{p_g} \right] \quad [1-11]$$

Here, p_g is the initial gas pressure in a bubble, p_m is the sum of atmospheric and acoustic pressures, γ is the heat capacity ratio of gaseous components inside the bubble, and T_0 is the ambient temperature. At the point of bubble collapse, high temperature and pressure will result in the liquid, giving rise to

effects such as molecular degradation, dispersion and erosion.

Since the early calculations of Rayleigh, the temperature of the collapsed bubble has been predicted by various hydrodynamic models to be as low as 1000 K and as high as 10,000 K [Raleigh, 1917]. Suslick and Hammerton [1986] for the first time measured experimentally the temperature of the collapsed cavity by using comparative rate thermometry. They determined two regions with temperature of ≈ 5100 K in gas phase inside the bubble, and ≈ 2000 K in a shell of liquid around the collapsed bubble [Suslick, 1985, 1986]. They derived the gas- and liquid-phase rate coefficients (k_g and k_l) from the observed first-order rate constants for the sonolysis of $\text{Fe}(\text{CO})_5$ vs its vapor pressure. The average effective temperature reached in each site was calculated from the Arrhenius expression. They used the activation parameters determined by high-temperature gas-phase laser pyrolysis in their calculations. These temperatures are of course dependent on the nature of the liquid, the bulk temperature etc.

Flint and Suslick [1991] have directly determined the sonoluminescence emission temperature of excited state C_2 produced during acoustic cavitation. The best computational fit to their raw data was at an emission temperature 5125 K, at 20 kHz in silicone oil under Ar with a vapour pressure of ≈ 0.01 torr.

It should be emphasized that one single temperature can not explain all aspects of cavitation. The local conditions inside the bubble are extraordinarily dynamic. The spatial and temporal temperature profile of a cavitating bubble is

consideration, as there is no thermal equilibrium during the cavitation process.

1.5.2.4 Resonance radius of the bubble

In stable cavitation, a bubble oscillates in size for several periods in an acoustic field. This oscillation can be carried out by bubbles with different sizes, but the greatest effect will occur for bubbles with a resonant radius. When the bubble contains gas with heat capacity ratio of γ and is in a liquid with density ρ at pressure p , then the resonant radius R_r in an acoustic field with radial frequency ω is:

$$R_r = \left(\frac{3\gamma p}{\rho \omega^2} \right)^{\frac{1}{2}} \quad [1-12]$$

CHAPTER 2

APPARATUS AND SONOCHEMICAL REACTOR DESIGN

2.1 Introduction

An ultrasonic apparatus must have a device capable of converting some form of energy into high frequency acoustic waves, i.e. a transducer. Ultrasonic transducers are designed to convert either mechanical or electrical energy into ultrasound. There are three main types of transducer: gas driven, liquid driven and electromechanical. The last type is the most common. Electromechanical transducers are based on either piezoelectric or magnetostrictive effects. Piezoelectric transducers are those most commonly used to power bath and probe type sonicator system.

2.2 Piezoelectric transducer

A thin plate of a crystal such as quartz (x-cut quartz) shows two complementary effects. The first one is the piezoelectric effect. When a physical pressure is applied on the surfaces of the thin plate, an equal but opposite charge is generated on each side. Polarity is reversed if tension is applied across the surfaces. This generation of an electrical potential on the crystal surfaces by mechanical stress was discovered in 1880 by the Curie brothers Pierre and Jacques. The second effect is the reverse piezoelectric effect. When an electrical potential is applied across the faces of the crystal, then there is a mechanical deformation of the crystal (expansion or contraction depending on the polarity of the applied voltage).

A piezoelectric transducer generally consists of a thin plate of

piezoelectric material such as quartz, barium titanate (BaTiO_3), lead metaniobate (PbNb_2O_6), the mixed crystal lead zirconate titanate, or several other ceramics. These plates are coated with thin metallic films on their faces, forming two electrodes. The front electrode, which is in contact with the liquid medium, is usually grounded to prevent shock. In continuous wave operation, an oscillating electrical potential is then applied to the back electrode to vibrate the crystal and produce ultrasonic waves.

It is not possible to vibrate a piezoelectric crystal plate at every frequency. Each crystal plate has an optimum performance at the natural resonance frequency, which is related to the crystal dimension. For example, a transducer with thickness of 2.88 mm (x-cut quartz) has a natural frequency of 1 MHz whereas for 0.288 mm it has a natural frequency at 10 MHz. This is a reason why any conventional ultrasonic equipment (bath or probe) has its own specific frequency.

2.3 Types of sonication

Ultrasonic waves can be introduced into a system directly or indirectly. The ultrasonic source can be put directly into the reaction medium, or a container with the system can be immersed in a tank containing a sonicated liquid (usually water).

In ultrasonic probe systems which sonicate a solution directly, the acoustic horn is the essential part for leading the acoustic energy from the

transducer to the reaction mixture. The amount of transferred energy is related to the shape of the horn. Horns magnify the vibrational amplitude by a factor which is dependent on the type of taper [Mason, 1988].

2.3.1 Sonication by the 20 kHz apparatus

The 20 kHz ultrasound was produced by a Vibra-Cell VC375 ultrasonic processor. The ultrasound was introduced directly into the sample solution through a titanium horn as in similar apparatuses described earlier [Kruus, 1987].

To improve the reproducibility of the sonication results, a plastic sleeve was constructed for connecting the reactant container to the horn in a reproducible manner. This technique also made it possible to control the gas present (Figure 2.1).

Three different horns with tip areas of 1.1 cm^2 (referred to as "small"), 2.48 cm^2 ("medium"), and a special horn provided by Vibra-Cell with a tip area of 8.04 cm^2 ("X-large") were used for determining the effect of intensity (W cm^{-2}) on the reactions.

2.3.2 Sonication by the 900 kHz apparatus

An apparatus was constructed which produces 900 kHz ultrasound through a flat transducer mounted at the bottom of a reaction vessel holding the solution. The details of the sonication cell are shown in Figure 2.2. The power

Figure 2.1: A plastic sleeve which connected the reactant container to the 20 kHz ultrasonic horn.

Figure 2.2: Sonochemical reactor which designed and constructed for 900 kHz apparatus.

A: transducer (EBL #1 (PZT-4) 2.125 in diameter from Staveley Sensors Inc, Connecticut), **B:** O ring (Buna-N), **C:** silver conducting epoxy cement (Chomerics), **D:** protective resin (RTV 11 white), **E:** reaction solution (typically 150 mL), **F:** circulating thermostating bath, **G:** lid (plastic), **H:** support frame (plastic), **I:** entry for thermocouple, **J:** inlet for gases (stainless steel tube with a perforated end), **K:** outlet for gases, **L:** stainless steel base.

amplifier for this apparatus was from an apparatus supplied by Meinhardt Ultrasonics, Leipzig, Germany (Figure 2.3). In this new apparatus the ultrasound can enter the system directly when the solution studied has a negligible effect on the RTV resin used in the apparatus. The sonication of aqueous potassium iodide solution can be carried out in this way for short periods. The ultrasound must be introduced indirectly when there is an effect between the reactants and RTV resin. In this case the position of the vessel inside the sonication cell is important.

A holder was attached to a standing device equipped with a micrometer, and then the reactant container was coupled to the holder. With this equipment it is possible to fix the position of the container with respect to the ultrasonic source at the same position in different runs (Figure 2.4).

During sonication, heat is dissipated in the solution. The sonication cell was thus equipped with a circulating water bath for controlling the temperature. In the case of low intensity, there was a good temperature control during the sonication with a temperature increase of about 2°C. At high intensity, however, there was a significant increase in the temperature of more than 10°C. A glass coil was thus constructed for inside the sonication cell such that it is immersed in the sonicated liquid. The temperature control of the system was thus improved owing to the cooling of the system from both outside and inside by a thermostat.

Figure 2.3: 900 kHz apparatus (power amplifier from an apparatus supplied by Meinhardt Ultrasonics and sonochemical reactors) and direct sonication.

Figure 2.4: *Indirect sonication by 900 kHz apparatus.*

2.4 Measurement of total acoustic power

The two common methods for measuring the acoustic power are through the use of the radiation force and through calorimetry.

In the radiation force method, the acoustic beam is directed to an absorbing or reflecting target. A microbalance can show the change produced by the radiation force. The following formula shows the relationship between the radiation force and other parameters:

$$F = D \frac{P}{v} \quad [2-1]$$

Here, p is the total acoustic power at the target point, v is the velocity of sound in the medium, and D is a constant depending on the design of the target and the shape of the acoustic field. The measurement of radiation force is rather easy to perform, but microstreaming produced around the target may cause some inaccuracy in the results.

The absolute measurement of acoustic power through calorimetric methods is based on determining the amount of heat produced by ultrasound. In this method, the acoustic beam is directed into an adiabatic chamber (e.g. a Dewar flask) filled with an absorbing liquid. By measuring the temperature rise of the liquid inside the Dewar, the total power can be calculated according to the following formula:

$$\text{Power} = m C_p \left(\frac{dT}{dt} \right) \quad [2-2]$$

where C_p is heat capacity of the liquid ($\text{J kg}^{-1} \text{K}^{-1}$), m is the mass of liquid used (kg), and dT/dt is the temperature rise per second at time zero (K s^{-1}). If this power (W) is dissipated into the system from a probe tip with surface area A cm^2 , then the intensity of power (W cm^{-2}) produced by the source of ultrasound can be determined.

The use of the calorimetric method for the case of 20 kHz is very easily done by simple immersion of ultrasonic horn into a dewar. Figure 2.5 shows the acoustic power calibration curve for 20 kHz. However, it is not possible to measure the acoustic power of 900 kHz by use of a dewar. For this measurement, the thermostat water was evacuated from the sonication cell (Figure 2.2) and then the temperature rise was recorded from inside the sonicated cell. It is clear that the loss of heat during the sonication at 900 kHz is more than from a Dewar at 20 kHz (Figure 2.6).

When the ultrasonic power setting on the generator is constant, the change in the reaction temperature results in a change in the sonochemical reaction rate. It should be emphasized that with changing the temperature the intensity also changes [Mason, 1992]. At a constant power setting, the acoustic power actually measured varies somewhat with temperature. The greatest variation of power with temperature was for the X-large horn: the

Figure 2.5: Acoustic power calibration curve for 20 kHz.

Figure 2.6: Acoustic power calibration curve for 900 kHz.

power is 33 watt at 5 °C and 34 watt at 50 °C when it is set to give 42 watt at 25°C [Entezari, submitted for publication].

2.4.1 Power calibration for indirect sonication

Acoustic power calibration for 900 kHz has been performed previously. Here the sample was sonicated indirectly; it is therefore necessary to determine the actual power which comes into the sample for sonochemical dissociation of carbon disulfide.

This calibration was performed by using the oxidation of potassium iodide. The total acoustic power with the 900 kHz apparatus was measured by calorimetry to be 29 W at room temperature. This produced 2.35 μmol iodine when 50 mL of iodide solution was directly sonicated for 3 minutes at 298 K. Indirect sonication of a 50 mL sample in an Erlenmeyer (125 mL) under the same condition produced different amounts of iodine depending on the volume of water used for a coupling medium. With 170 mL water, 1.40 μmol iodine was produced in 3 minutes; with 100 mL water, 1.63 μmol ; and with 75 mL water, 1.93 μmol .

These differences might be due to differences in the mass of sonicated liquid. It means that vibration of larger amount of water is more difficult than smaller one. In another way, in the presence of fluid loading, the applied force encounters the sum of the mechanical impedance of the source and the radiation impedance of the fluid. The mechanical impedance of the sonicator is

increased by the load of the medium and the radiation impedance is also increased by increasing the mass of the medium [Kinsler, 1982].

It should be mentioned that the position of Erlenmeyer with respect to piezo-ceramic transducer was constant in all experiments (≈ 1 cm above the transducer). As our experiments were done with about 100 mL water as a coupling medium, it is possible to conclude that the actual power which came to the sample was about 20 W. This means that around two thirds of the acoustic power was transmitted to the sample.

CHAPTER 3

SONOCHEMICAL DISSOCIATION OF WATER IN POTASSIUM IODIDE SOLUTION

3.1 Introduction

The major products from the ultrasonic irradiation of water itself are H_2O_2 and H_2 . Various data suggest that the initial step is the cleavage of water to form radicals. Various inorganic and organic compounds have been subjected to ultrasonic irradiation either as aqueous solutions or as suspensions in water. Since extremely reactive species ($\text{H}^\cdot$ and $\text{OH}^\cdot$) formed from the sonolysis of water itself (homolytic cleavage), a wide range of secondary sonochemistry in aqueous solutions can be expected; this has been repeatedly observed.

3.1.1 Sonolysis of aqueous solutions

The first homogeneous sonochemical experiments showed that reactive species such as $\text{H}^\cdot$, $\text{OH}^\cdot$, H_2O_2 were formed during ultrasonic irradiation of water [Lindstrom, 1951; Del'Duca, 1958; Weissler, 1959; Lippit, 1972]. The first suggestions of the mechanism for this reaction were made already in 1951 by Lindstrom. Riesz and co-workers [1985] were able to observe the highly reactive radicals produced during cavitation by using spin traps. The radicals formed in the sonolysis of water are capable of causing secondary oxidation and reduction reactions, in this case the oxidation of iodide to iodine.

The reactions postulated to take place in such a system are summarized below. The primary reaction is known to be:

In presence of air, the O_2 molecule can act as a scavenger, and:

Another radical reaction can take place:

The final reaction observed through visible spectroscopy is:

The hydrogen molecule and hydrogen peroxide are also produced by the sonolysis of aqueous solution. They are formed by the combination of H atom and OH radicals respectively. The products, i.e. H_2O_2 and I_3^- , can react in neutral or alkaline solutions:

According to Henglein [1991], the concentration of H_2O_2 produced by sonication of 0.200 M aqueous potassium iodide solution is very low. Therefore, the rate of reaction [3-5] should be negligible.

3.1.2 Frequency effects

Lorimer [1990] noted that ultrasound at higher frequencies is attenuated more rapidly than that at lower frequencies. He concluded that this is the reason why most sonochemistry is traditionally performed in the low frequency (20-50 kHz) region. Only a few researchers, e.g. Henglein [1993], have used higher-frequency apparatus for studies of sonochemical reactions.

Cum et al [1992] have investigated the effect of frequency in the range of 20-80 kHz on the oxidation of iodide to iodine. They ascertained that there is an intermediate frequency (59 kHz) which is capable of driving a sonochemical reaction at its maximum rate.

Weissler [1950] has also examined the effect of frequency on the oxidation of iodide in the range of 400-1500 kHz. He noted an irregular variation in iodine yield with increasing frequency at constant power input. He attributed this not to an intrinsic frequency sensitivity of the reaction, but rather to variation of the transparency of the test-tube containing the reacting solution with the frequency of the ultrasound used.

The effect of frequency on the rates of sonochemical reactions has thus not been explored carefully in the literature. This work represents the results of experiments where the absolute sonochemical rates at two widely differing frequencies (20 and 900 kHz) are compared. In order to make an absolute comparison, a new high-frequency ultrasonic apparatus suitable for sonochemistry was designed and constructed.

3.2 Experimental procedures

3.2.1 Experiments at 20 kHz

In a typical experiment, 150 mL of aqueous potassium iodide solution (0.2 mol L^{-1}) was poured into a vessel designed specifically for 20 kHz sonication. The vessel was fixed by an adaptor to the horn, so that the position of the cell relative to the horn was exactly reproducible. The vessel was then immersed in the bath and allowed to reach thermal equilibrium. All experiments were done at $30 \pm 3^\circ\text{C}$ unless otherwise indicated. This temperature was reached after 5 minutes of sonication. This procedure was used for the data presented in Figures 3.1, 3.2, 3.3, 3.4 and 3.5.

In another series of experiments (other Figures), 100 mL of aqueous potassium iodide solution (0.2 mol L^{-1}) was poured into a Rosette cell for sonication with 20 kHz using different horn sizes. The position of different horns was the same with respect to the Rosette cell. The runs were done under a normal atmosphere with no gases bubbled through the solution, unless otherwise indicated.

After sonication for a selected time, the intensity of color due to the production of iodine was measured by a Beckman DU-7 spectrophotometer at 355 nm. It should be noted that a new solution was used to obtain data for each point in the iodine vs time graphs (see Figure 3.1). Removing portions of sample changed the volume sufficiently to cause differences. In the examples of the experimental results shown in Figure 3.1, the standard deviations of the

Figure 3.1: Sonication of aqueous solutions of potassium iodide (0.2 mol L^{-1}), 303 K, 39 Watt acoustic power, 20 kHz. ■ : in the presence of air, ○ : in the presence of Ar

averages of between 3 and 7 determinations of each point are shown.

In some experiments, a gas (e.g. argon) was bubbled into the solution for 15 minutes before sonication through a side-arm mounted on the cell. The solutions were then irradiated.

3.2.2 Experiments at 900 kHz

The conditions and experimental procedures for 900 kHz were the same as 20 kHz, with the solutions irradiated directly as in the case of 20 kHz. The sonochemical rate was not sensitive to a change in volume with this frequency. An example of a rate determination is shown in Figure 3.2. Sonication with 900 kHz was under a normal atmosphere, except for some runs where an argon atmosphere was maintained and others for which degassed solutions were used. In order to improve the temperature control in the reaction solution, a coiled glass tube was immersed in it. Water from the thermostat was directed through this tube.

Each rate was obtained from the slope of a plot of absorption at 355 nm vs time using four or five data points. The reproducibility of the rate data was generally better than 5%. Limits of uncertainty are shown in the figures for data with greater imprecision. During a rate determination, the temperature varied somewhat depending on the acoustic power. At low power, it was $\pm 1\text{ }^{\circ}\text{C}$ during a run, while at the highest power it could vary up to $\pm 10\text{ }^{\circ}\text{C}$.

The behaviour of the solutions during sonication differs markedly at 900

Figure 3.2: Sonication of aqueous solutions of potassium iodide (0.2 mol L^{-1}), 303 K, 25 Watt acoustic power, 900 kHz. ■ :in the presence of air, ○ :in the presence of Ar

kHz. There is no cavitation noise to be heard; at 20 kHz, this could be very harsh and irritating to the ears even with ear protection. Any cavitation bubbles that were visible were also much smaller, and very few migrated to the top of the solution to leave it.

3.3 Results and discussion

3.3.1 Primary experimental data

The types of primary data obtained are shown in Figures 3.1 and 3.2. Each point in these graphs is the average of at least 3 determinations. Note that in all cases for 20 kHz, only one point was taken per run, as the results were sensitive to any variation of solution volume. The geometry was kept the same for all runs, as data also varied with position of the ultrasound source relative to the reaction vessel.

The results obtained for the oxidation of iodide to iodine under argon or air by ultrasonic sonication at two different frequencies are summarized in Table 3.1. These data are derived from the graphs shown in Figures 3.1 and 3.2.

Figure 3.3 emphasizes the large frequency effect possible in the rate of sonochemical oxidation of aqueous iodide in the presence of air (experiments 1 and 2 in Table 3.1).

Figure 3.3: *Effect of frequency on the sonochemical oxidation of iodide in the presence of air.* ■ :900 kHz, ◆ :20 kHz

Table 3.1: The rate is in units of $10^6 \text{ mol I}_2 \text{ h}^{-1} \text{ W}^{-1}$.

Exp. No.	ν / kHz	Gas	Rate	Ratio
1	20	air	7.1 ± 0.5	2:1 = 31
2	900	air	$219. \pm 7$	2:4 = 3.1
3	20	Ar	8.1 ± 0.5	1:3 = 0.9
4	900	Ar	$70. \pm 0.8$	4:3 = 8.6

3.3.2 Basic considerations

Several factors are likely to be influential in determining the effectiveness of cavitation produced by ultrasound in promoting chemical reactions.

It is visually apparent that the size of the cavitation bubbles are different at the two frequencies. The cavitation bubbles whose collapse causes the initiating reaction [3-1] will be of varying sizes. Their radii are however likely to be of the order of the radius of a bubble resonant in the applied acoustic field (Equation 1-12). For 20 kHz, R_r at 300 K in water is $164 \mu\text{m}$, while for 900 kHz it is $3.6 \mu\text{m}$. There is thus a vast difference in the sizes of the cavitation bubbles present at 20 kHz as compared to 900 kHz.

The rate of heat transport out of a bubble is dependent on the surface area, i.e. larger (20 kHz) bubbles would lose energy at a greater rate. The rate that the temperature drops is however dependent on the surface to volume ratio. As this ratio varies as the reciprocal of the radius, the smaller 900 kHz bubbles should cool more rapidly than the larger 20 kHz bubbles after being

heated during compression.

The temperatures reached and maintained in cavitation bubbles also depend on temporal characteristics, as well as the spatial aspects discussed above. Some of these characteristics are summarized in Table 3.2. It is obvious that the rate of contraction and expansion of a bubble in a 900 kHz acoustic field is much greater than at 20 kHz (Table 3.2).

The collapse time for the cavitation bubbles can be calculated from equation [1-8], and the collapse pressure is the sum of the hydrostatic and the acoustic pressure. The values used are given in Table 3.2.

The collapse time calculated from [1-8] for 900 kHz bubbles is less than for 20 kHz, but by a ratio of 23, rather than 45, the ratio of frequencies. The collapse is primarily inertia-driven, and is not affected to any great extent by the acoustic pressure variations present. The time available for transport of heat out of the collapsing bubble is thus about 20 times more for a 20 kHz cavity compared to one at 900 kHz. The calculated collapse times as shown in Table 3.2 are of the order of microseconds. However, collapse times of the order of picoseconds have been reported in the literature [Barber, 1991].

Table 3.2: Comparison of temporal and spatial characteristics of cavitation bubbles with frequency in water at 300 K.

v/kHz	Period time / μs	p(collapse) / atm	t(collapse) / μs	R_c / μm
20	50	11.2	4.5	164
900	1.1	2.9	0.19	3.6

The difference in the noise caused by collapse of the cavitation bubbles is very noticeable. There is essentially no noise in the audible range with 900 kHz irradiation, while the noise with 20 kHz is loud, harsh and irritating. This suggests that the nature of the cavitation may have considerable differences. It may be that there is more transient cavitation occurring at 20 kHz, and more stable cavitation at 900 kHz.

In the case of this reaction, resonant (stable) cavitation might not produce temperatures high enough to cause significant dissociation of the water molecules. The temperatures reached can be described in an idealized system according to the equation [1-11]. It has been shown that resonant cavitation can give rise to temperatures of 1,800 K [Saksena, 1970]. This is still rather small as compared to the "characteristic temperature" (bond energy/R) of 60,000 K for the breaking of an O-H bond (498 kJ mol⁻¹).

A transient collapse can cause temperatures in the cavities of the order of 5,000 K and the surrounding liquid of the order of 2,100 K [Suslick, 1986]. The factor $\exp\{-(\text{bond energy})/RT\}$ that can be achieved at 5,000 K is thus of the order of 6×10^{-5} , i.e. a significant fraction of the molecules would have sufficient energy for dissociation.

3.3.3 Variation with power

The variation of the rate with acoustic power is shown in Figure 3.4. In the case of the 900 kHz, the rate is linear with power in the range available

Figure 3.4: Variation of sonochemical rates with acoustic power. Aqueous potassium iodide (0.2 mol L^{-1}), $303 \pm 6 \text{ K}$, ■ : 900kHz, ♦ : 20 kHz.

experimentally, and there is a clear cavitation threshold at 3 watt ($0.14 \text{ watt cm}^{-2}$). Most experiments were done with a power of 25 watt, corresponding to 1.2 watt cm^{-2} . In the case of 20 kHz, there are traces of cavitation on parts of the surfaces of the 20 kHz tip even at the lowest possible settings, so that a clear cavitation threshold is not evident.

It is evident from Figure 3.5 that the variation of the rate at 20 kHz is not linear with power. At higher power, the reaction rate per unit power drops off, most likely because a large fraction of the visible bubbles migrate out of the solution. Many bubbles can be seen close to the transducer tip. These must interfere with the introduction of ultrasound into the liquid. This is a possible explanation of the "saturation" of the sonochemical effect at higher powers. A small part of the nonlinearity is probably due to a variation in solution temperature with power.

The tip used in most experiments had a surface area of 1.1 cm^2 , so that at a power of 39 watt, there was 36 watt cm^{-2} . It is obviously necessary to investigate the effect of power density (intensity) rather than power alone by using ultrasonic sources with different area. The areas were 1.1 and 21 cm^2 for the 20 and 900 kHz apparatus respectively. It is possible that there is a dependence of the rate on power density as well as on total power. As shown in the following, for the reaction studied here, sonolysis seems to be more effective at lower power densities, with total power kept constant.

The variation of the reaction rate with acoustic power at 20 kHz is shown

Figure 3.5: Variation of sonochemical rates with acoustic power at 20 kHz (Fig. 3.4) on an enlarged scale.

in Figure 3.6 for the three tip sizes available. It is evident that the variation is not linear with power. The non-linearity of the rate vs power relation decreases with increase in the tip size, i.e. decrease in the intensity.

3.3.3.1 Effect of tip size (intensity)

Table 3.3 summarizes the effect of tip size on the rate of iodide oxidation. According to this table the rate is greatest with the X-large tip, i.e. with the lowest intensity. This table gives data for cases when the power is of the order of 40 watt. The generality of the dependence of the rate with tip size can be seen in Figures 3.6 and 3.7. The data in Figure 3.7 was obtained with power settings which gave 42 watt at room temperature. A correction for this power variation is shown for the X-large horn (Figure 3.7). As seen in Figure 3.6, the sonochemical rate varies essentially linearly with power for that horn, so that such a correction is reasonably easy to make.

In the case of the 900 kHz, the rate is linear with power in the range available experimentally (Figure 3.8). There is also a clear cavitation threshold at 8 watt ($0.37 \text{ watt cm}^{-2}$) at 5 °C.

Figure 3.6 also shows that the curves become increasingly linear with increasing horn tip area. With 900 kHz the irradiation area is larger, giving an even lower intensity. As can be seen in Figure 3.8, the rate is linear with power.

The reasons for these results must be related to the cavitation bubble

Figure 3.6: Variation of the rate of sonochemical oxidation of iodide vs power at $20 \pm 5^\circ\text{C}$ with different horns. Each point is the average of at least two independent determinations, with an estimated reproducibility of $\pm 3\%$.
● small tip (1.10 cm^2); ♦ medium tip (2.46 cm^2); ■ X-large tip (8.04 cm^2).

Table 3.3: The variation of the sonochemical reaction rate (in $\mu\text{mol h}^{-1}$) at 20 kHz at $5 \pm 3^\circ\text{C}$ with different horns.

Tip type	Size cm^2	Power W	Intensity W cm^{-2}	Rate $\mu\text{mol h}^{-1}$
Small	1.10	38.	34.	2.7
Medium	2.46	37.	15.	7.1
X-large	8.04	36.	4.5	12.7

Figure 3.7: Variation of the rate of sonochemical oxidation of iodide vs temperature at 20 kHz with different horn tips. ● small tip (1.10 cm²); ♦ medium tip (2.46 cm²); ■ X-large tip (8.04 cm²). The power was in each case set to be 42 ± 2 W at room temperature. It was however as much as 20 % less at the lowest and highest temperatures. A correction for this power variation is shown for the X-large tip -□-- . Each point is the average of at least two independent determinations, with an estimated reproducibility of ± 3%.

Figure 3.8: Variation of the rate of sonochemical oxidation of iodide with power under 900 kHz irradiation at 5 °C, where the 20 kHz effect is greatest. are points from the experimental data in Fig. 3.10; shows the rate at the same power and temperature with 20 kHz irradiation using the X-large tip.

field which appears under the tip of the 20 kHz horns. It can be seen to differ markedly with the tip area (Figure 3.9).

The number of cavitation bubbles (i.e. reaction sites) present is important in the efficiency of the reaction. A larger horn produces more bubbles since it can contact a larger surface area of liquid. It therefore also irradiates a larger volume of liquid.

Bubble interaction is also important in affecting the rate of the reaction. In the case of a larger horn, the collision probability of bubbles is lower, leading to a lower probability of combination of bubbles, forming larger bubble which float away to the surface of the liquid. Such large bubbles do not contribute to chemical activity. When a larger horn is used, the irradiated volume of liquid thus loses fewer chemically ineffective bubbles during sonication.

As can be seen in Figure 3.10, at very high intensities, the application of more power may be counterproductive. There are so many large cavities under the tip that the contact between tip and liquid is poorer, and the acoustic energy is dissipated to a greater extent into heating the horn.

Intensity is a very important factor. As indicated, irradiation at two different intensities can give completely different results.

3.3.4 Variation with gas

The oxidation of potassium iodide in aqueous solution is 1.1 times greater with argon than with air at 20 kHz (see Table 3.1). This can be

Figure 3.9: *A picture of the two horns with different tip size (20 kHz).*

explained through the greater heat capacity ratio for argon as compared to air, together with the greater heat conductivity of air as compared to argon. The implosion of bubbles with argon produces a higher temperature [Equation 1-11], and this thermal energy is dissipated more slowly. Table 3.1 also shows that the rate of oxidation is smaller by a factor of 0.3 with argon compared to air with 900 kHz.

Table 3.4 also shows the change in the sonochemical rate under different conditions of gas. The reaction rates with argon present are definitely lower at 900 kHz. The data in Table 3.4 also includes the results for solutions which were degassed by freeze-pump-thaw cycles. The rate with 900 kHz irradiation in a solution made up with water which had been boiled for 10 min and subsequently cooled was also $62 \mu\text{mol h}^{-1}$.

It was not possible to measure the actual gas content in such "degassed" solutions. Some authors have reported that they still contain considerable amounts of gases after the degassing procedure [Pickworth, 1988].

Table 3.4: Variation of the sonochemical reaction rate ($\mu\text{mol h}^{-1}$) with 20 kHz (X-large tip, 70 W) and 900 kHz (76 W) irradiation with different gas conditions. The degassing was done through three freeze-pump-thaw cycles. (B) indicates bubbling for 20 min before sonication; (B&D) indicates bubbling before and during sonication. The data are the averages of at least two determinations.

Frequency	Air	Degassed	Argon (B)	Argon(B&D)
900 kHz	$92. \pm 1.$	$62. \pm 2.$	$20. \pm 2.$	$32. \pm 0.5$
20 kHz	14.	9.5	$47. \pm 0.6$	46.

With 20 kHz irradiation, the reaction rate in a degassed solution is lower than in an aerated solution. However, the rate with argon present is greater than with air, and independent of whether there is continuous introduction of argon. The nature of the gas present does therefore affect the reaction rate, and any degassing during ultrasonic irradiation does not seem to be significant.

The gas affects the ratio of specific heats and the thermal conductivity of the bubble contents. When O_2 is present, then it can also participate in the reactions that can occur inside the cavitation bubble.

As can be seen in Table 3.4, the order of the rate with 20 kHz is: argon > air > degassed, while with 900 kHz it is air > degassed > argon. This difference between the 20 and 900 kHz results can be explained according to the radical reactions proposed by Petrier [1992]. The collapse time of bubbles in a 900 kHz acoustic field is shorter than with 20 kHz. In the presence of air, reaction [3-2] reduces the back reaction of reaction [3-1]. Therefore the concentration of hydroxyl radicals is greater with air than with argon. We can conclude that the rate of oxidation with air is greater than with argon with 900 kHz. But in the case of 20 kHz, the collapse time of bubbles is enough for reaction [3-3] to occur. This reaction reduces the concentration of hydroxyl radicals; therefore the rate of oxidation with air will be lower than with argon at 20 kHz. One of these possible secondary reactions was the scavenging of $H^\cdot$ with O_2 to form $OOH^\cdot$.

A considerable amount of gas may be left in the degassed solutions

[Pickworth, 1988], so that there is still likely to be some O_2 available for the above scavenging reaction. The rate in a degassed solution would thus be expected to be intermediate between the argon and the air, as is the case with 900 kHz.

The low rate of reaction in degassed solutions using 20 kHz ultrasound also might be due to a fewer nucleation sites.

3.3.5 Variation of sonochemical rate with frequency

In the new 900 kHz apparatus, the rate of oxidation was much faster (more than 30 times) than in the 20 kHz apparatus (see Table 3.1 and Figure 3.3).

It was thought that the increased rate may be related to the standing waves which may form from the reflection of the ultrasound from the solution surface. This was examined by placing a plate on the surface and varying its position using a micrometer by amounts less than the wavelength of 900 kHz ultrasound in water (1.7 mm). The results showed that standing wave can not be a reason for this increase in the oxidation rate.

The tip area of ultrasonic irradiator is another parameter which certainly has an effect on the rate of reaction. We tried to provide the same conditions for both apparatuses (20 and 900 kHz), but there was an intrinsic difference between them, the surface area of ultrasonic irradiator. The surface area for 900 kHz was 21 cm^2 and for 20 kHz at most 8.04 cm^2 . Even when the total

power was the same, the power per surface area (intensity) was considerably different.

Figure 3.8 (p. 70) shows the rate of oxidation versus acoustic power with 900 kHz under the same conditions as with 20 kHz. It is possible to interpolate to the rate for a power of 37 W, for which data with 20 kHz irradiation is available in Table 3.3. The rate is $40 \mu\text{mol h}^{-1}$. Extrapolation of the data in Table 3.3 to a tip size of 21 cm^2 gives a rate of between 20 to $30 \mu\text{mol h}^{-1}$, depending on the type of extrapolation (linear or polynomial).

With this method we can estimate the rate of oxidation of iodide with 20 kHz with a tip area equal to the 900 kHz apparatus. Comparison the results shows that the real effect of frequency on the oxidation rate is 1.3 to 2 times greater with 900 kHz than with 20 kHz.

Why is the sonochemical reaction rate greater at 900 kHz than at 20 kHz? Some reasons for this may be the following:

The transformation of acoustic energy to thermal energy in the regions of chemical activity may be more efficient in the 900 kHz apparatus. It is obvious that less energy is being lost at 900 kHz through large bubbles floating to the top, as observed in the 20 kHz apparatus. There may be many more cavitation bubbles ("mini-reactors") of appropriate size at 900 kHz.

It is in this case unlikely that the resonant cavitation which seems to be more prominent at 900 kHz may be more effective in dissociating the water molecules. Resonant cavitation is more effective for the initiation of

polymerization [Kruus, 1991], but this is only because transient cavitation produces "hot spots" which have such a high temperature that undesirable pyrolysis reactions occur. In the oxidation of iodide, the only initial reaction possible is the dissociation of water.

In addition, the temperature variation is definitely dependent on the irradiation frequency. The reason for this dependence is however not readily explained. It may be due to the spatial and temporal characteristics of the cavitation processes occurring at the two frequencies. For constant power, a larger irradiation surface (lower intensity) and a higher frequency provide more cavitation bubbles which act as "mini-reactors".

3.3.6 Variation with temperature

The sonochemical reaction rate of oxidation of iodide was measured at different temperatures (0-50 °C) with different ultrasonic horns at low frequency (20 kHz), and with high frequency (900 kHz) apparatus.

Figure 3.10 shows the results with 20 kHz irradiation using the X-large tip horn. As the temperature of the solution is increased, the reaction rate generally decreases. The shape of the rate vs temperature relation is however dependent on the power.

At sufficiently high power, there is no further increase in the reaction rate with power. This is in agreement both with other sonochemical reactions such as the initiation of polymerization [Patraboy, 1985], and with evidence from

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Figure 3.10: Variation with temperature of the rate of sonochemical oxidation of iodide using 20 kHz irradiation with an X-large tip. ▲ 21 watt; + 32 watt; ◆ 42 watt; ● 56 watt; ▼ 72 watt. Each point is the average of at least two independent determinations, with an estimated reproducibility of $\pm 3\%$. The power data indicated are those measured at room temperature. The power can be as much as 20% less than this at 0 and 50 $^{\circ}\text{C}$, a correction for this does not change the basic shapes of the curves (see figure 3.7 for an example of the magnitude of the correction). For easier viewing, the points are joined by curves which are third order polynomial fits.

sonoluminescence experiments [Didenko, 1991].

In contrast, as seen in Figure 3.11, with irradiation at 900 kHz, the reaction rate shows a maximum at a temperature intermediate between 5 and 50 °C in this system, dependent on power level. Only four discrete power settings were available with the 900 kHz equipment, and since the lowest produced negligible reaction, only three curves are available.

At a specific setting, the power output of both pieces of equipment varied somewhat with temperature, more significantly with the 20 kHz apparatus. Such variation is however not sufficient to change the general shapes of the curves in Figures 3.10 and 3.11 (Figure 3.7 shows the magnitude of the correction).

3.3.6.1 Effect of temperature: general considerations

In a discussion of temperature effects, it must be remembered that there is a temperature dependence for the initial reaction caused by the collapse of the cavitation bubble. Subsequent reactions, both those which interfere and those which lead to the final product (here I_3^-), are however also temperature dependent.

The primary reaction taking place in such a system is believed to be the reaction [3-1], and the final reaction observed through visible spectroscopy is the reaction [3-4]. As explained below, rate of the primary reaction could increase or decrease with temperature; rates of all subsequent reactions should

Figure 3.11: Variation with temperature of the rate of sonochemical oxidation of iodide using 900 kHz irradiation.

● 7 watt; ◆ 25 watt; ■ 76 watt (measured at room temperature). Each point is the average of at least two independent determinations, with the estimated reproducibilities shown. The power varies at most $\pm 10\%$ from 0 to 50 °C from that measured at room temperature. For easier viewing, the points are joined by curves which are third order polynomial fits.

increase with temperature.

The temperatures reached in the collapse of a cavitation bubble can be described in an idealized system as the equation [1-11].

As the temperature of the liquid is increased, its vapour pressure is also increased, but much more dramatically than the temperature. As a result the final temperature of a collapsing cavity is decreased. The vapour which enters the bubble during its formation cushions the collapse of the bubble. This "vaporious" or "transient" cavitation is expected to be the predominant effect when little dissolved gas is present. This predicts that as the bulk temperature increases, the temperature of the "hot spot" formed by the cavity collapse decreases. As a result the rate decreases as bulk temperature increases.

When there is abundant gas present, then the cavitation is more likely to be "stable" or "gaseous". Contrary to "vaporious" cavitation, the effective Arrhenius activation energy should in this case not be negative. By changing the solution conditions, it is thus possible to obtain different chemical environments during the collapse of a cavitation bubble.

3.3.6.2 Effect of temperature: low frequency

The noise given off by the cavitation at 20 kHz suggests that there is more likely transient (mixture of vapour and gases) cavitation occurring. This is confirmed by the decrease in the reaction rate with temperature.

A possible explanation of the temperature effect at 20 kHz would thus be

that the solution is somewhat degassed by the formation of large bubbles which rise to the surface. With an increase in the temperature, both the amount of gas (lower solubility at high temperature) and vapour pressure are increased. Therefore, the composition of the bubble content is varied from the high ratio of p_{gas}/p_w at low temperature to the low ratio at high temperature. It means that the final temperature in the collapse of a cavity is lower at higher temperature than at lower temperature owing to the presence of much more vapour inside the bubbles. This explanation is also consistent with the experimental data presented in Table 3.4.

3.3.6.3 Effect of temperature: high frequency

The quiet nature of the 900 kHz cavitation suggests a more stable (mixture of vapour and gases) cavitation. This may however be to a large extent because the sub-harmonics at this higher frequency are above the normal hearing frequency threshold. The increase in the rate with temperature, at least at lower temperature and low power, also suggests that vaporous cavitation is not as predominant.

With 900 kHz, there is a maximum in the rate vs temperature relations at each power in Figure 3.11. An increase in the power moves this maximum toward a lower temperature. The maximum may even disappear at powers higher than those available in our laboratory.

The shapes of the curves at 900 kHz (Figure 3.11) can be explained by

the ratio of partial pressures p_{gas}/p_w inside the bubble. In the section of the curves where the rate is increasing (low temperature, lower power), the vapour pressure of water is lower and the solubility of gas higher. At low intensities, there are fewer bubbles which can rise to the surface so that there is enough gas to make p_{gas}/p_w large enough to give the cavitation a more "gaseous" nature, i.e. no decrease in rate with temperature. The collapse is sufficiently intense to produce enough $OH^\cdot$ [3-1]; increasing the temperature thus causes an increase on the final reaction [3-2].

In contrast, at higher temperatures and higher intensities, there is less dissolved gas, and more cavitation bubbles may be formed. The vapour pressure of the water is also greater. Thus p_{gas}/p_w is smaller and the cavitation has a more "vaporous" nature, i.e. a decrease in the rate is expected with an increase in temperature. The collapse would be not be as intense as that at lower temperature; the concentration of $OH^\cdot$ [3-1] would decrease as the temperature is increased.

According to the experimental results, we can conclude that the negative effect on the reaction rate of the decreasing concentration of $OH^\cdot$ [3-1] with increasing temperature is greater than the positive effect of temperature on the rate of subsequent reactions leading to the final products [3-2]. Therefore, the rate should be decreased at high temperature and intensities.

These results are supported by the data of both Didenko et al [Didenko, 1994] and Pickworth et al [1988], even though these have been considered

contradictory. Didenko et al. [1994], used 1.1 MHz ultrasound with an intensity of 10 W cm^{-2} to measure the sonoluminescence intensity at various temperatures. They found the sonoluminescence to decrease with temperature, in agreement with the majority of the previous results. Pickworth et al. [1988], using 1 MHz ultrasound obtained seemingly contradictory results, as there was an increase in sonoluminescence with temperature in the range of 22-45°C. However, Pickworth et al. [1988], used a much lower ultrasound intensities 1 and 3 W cm^{-2} .

3.4 Conclusions

The major aspect of this work is to demonstrate a new high-frequency sonochemical apparatus and to show that it is more effective in accelerating the rate of at least one chemical reaction. The effect of gas in high frequency is different than low frequency . These surprising results are difficult to explain on the basis of current understanding of the fundamentals of cavitation and sonochemistry.

Many questions are left unanswered: Is this a general phenomenon? Or is it something valid only for homogeneous reactions? Or are these observations specific only to the reaction we chose for our initial study?

The major contribution of this chapter is also to emphasize that there is considerable potential in increasing the efficiency of sonochemical reactions. The reaction conditions can be optimized by changes which may seem counter-

intuitive. It may be better to: (i) use a higher frequency; (ii) increase the irradiation area, decreasing the intensity; (iii) introduce some gas; and (iv) decrease the temperature in case of high intensity.

These "rules of thumb" may however not be generally valid. There is also uncertainty about the fundamental reasons for these trends. More research on heterogeneous and other homogeneous reactions is required to assess the generality of these results.

The evidence we have presented suggests that the geometry of the apparatus and the method of introducing the ultrasound are of importance, but that these are not the primary aspects responsible for the greater effectiveness of the 900 kHz irradiation. There seems to be a dependence of the reaction rate on irradiation frequency arising from the temporal and spatial characteristics of the cavitation bubbles produced.

The results do however indicate some very obvious advantages for studying and utilizing sonochemistry at a higher frequency: a higher reaction rate, better reproducibility, and less noise.

CHAPTER 4

SONOCHEMICAL DECOMPOSITION OF MONO-CHLOROBENZENE IN DILUTE AQUEOUS SOLUTIONS

4.1 Introduction

Aromatic compounds are stable and common contaminants of waste water in chemical industries. There are some traditional methods for destroying or eliminating of these organic contaminants from aquatic ecosystems such as ultrafiltration, extraction and incineration. Some relative new techniques such as photochemical [Ollis, 1989], supercritical [Thonton, 1992] and ultrasonic methods [Kotronarou, 1991; Serpone, 1992; Berlan, 1994] have been investigated regarding to the decomposition of these undesired compounds. The last method is a strong alternative to the other methods as it can be carried out easily and under mild conditions.

Cavitation produced by sonication brings about instantaneous local high temperature and pressure in liquid [Flint, 1991]. These rather extreme conditions are very short lived, but have been shown to produce several reactive species in aqueous systems such as $\text{OH}^\cdot$ and $\text{H}^\cdot$ [Riesz, 1985]. Therefore, sonolytic decomposition of pollutants might be related to the thermal decomposition in cavitation bubbles or reactions by OH radicals or H atoms.

Chlorinated hydrocarbons are persistent in the environment owing to their resistance to decomposition. These compounds have attracted a public attention due to the pollution of ground and river water by them [Kerfoot, 1987].

Zechmeister and coworkers [1955] showed that the sonication of a mixtures of halobenzene, halothiophene and halofuran in a silver nitrate solution led to precipitation of silver halide that contained some silver acetylide and

diacetylide. Other aromatic and heterocyclic rings can be cleaved by ultrasonic irradiation [Zechmeister, 1956].

Sonolysis of some chlorinated hydrocarbon such as methylene chloride, carbon tetrachloride, 1,1,1-trichloroethane and trichloroethylene [Cheung, 1991; Inazu, 1993], and chlorophenol [Gondrexon, 1993] in aqueous solutions have been studied. The reaction mechanism and decomposition products have not completely been elucidated [Cheung, 1991].

The aim of this work is to study the decomposition of chlorobenzene in dilute aqueous solution by ultrasonic irradiation at two different frequencies (20 and 900 kHz). This study also deals with the ultrasonic degradation under different intensities at a constant power with changing the tip size area.

4.2 Experimental procedures

A dilute solution of chlorobenzene was prepared by adding 0.200 mL chlorobenzene (Fisher) into de-ionized water in a one liter volumetric flask. This solution was stirred for several hours by a magnet.

The ultrasonic irradiation of aqueous solution of chlorobenzene was carried out in a Vibra-Cell VC375 that was operated at 20 kHz with a power of 35 Watts (Power Position = 5) at zero degrees. Sonication with this apparatus was done with two different horn sizes (1.1 and 8.04 cm²) at the same power. The reaction vessel was a cylinder glass containing 50 mL of aqueous solution which immersed into a ice bath. Another sonicator was the newly designed 900

kHz apparatus with a power of 33 Watts (Power position = 3) at zero degrees. In this case the reaction vessel was a 125 mL Erlenmeyer containing 50 mL of aqueous solution which sonicated indirectly at zero degree. These sonications were carried out under an air atmosphere.

Sonication of this solution resulted in the formation of a yellow color with a maximum absorption at wavelength of 253 nm (Figure 4.1). The sono-degradation was monitored at intervals by measuring the intensity of the yellow color by a Uv-Visible spectrophotometer (Perkin-Elmer, Lambda 4B); by the concentration of the chloride ion which was measured with a Dionex 4000i ion chromatography unit with a Dionex AS4-A column. The IC eluents were 1.7 mM NaHCO_3 and 1.8 mM Na_2CO_3 . The pH of the solution was monitored by a digital pH meter.

4.3 Results

The variation of the decomposition rate of chlorobenzene in water with two different tip sizes at 20 kHz was followed by the formation of chloride anion (Figure 4.2) and the intensity of yellow solution (Figure 4.3). Both measurements confirmed that the rate of dissociation is larger with the larger tip. It means that lower intensity (X-large horn) is more effective than higher intensity (small horn) under the same power. This comparison was done under the same conditions and the only variable was the size of the tip. The results in Figures 4.2 and 4.3 were obtained with the power setting at position 5 (35 W)

Figure 4.1: *Uv-Visible spectrum of yellow solution produced by sonodissociation of chlorobenzene in a dilute aqueous solution.*

Figure 4.2: Chloride anion concentration (ppm) vs sonication time.

+ 20 kHz with small horn, ● 20 kHz with X-large horn,
 ◆ 900 kHz. An estimated curve -.- for the case of 20 kHz with horn the
 same size as 900 kHz (21 cm²).

Figure 4.3: Absorbance of the yellow solution vs sonication time.
 + 20 kHz with small horn,   ● 20 kHz with X-large horn,
 ♦ 900 kHz. An estimated curve —•— for the case of 20 kHz with horn the
 same size as 900 kHz (21 cm²).

for both horns and the temperature was set at zero degrees. For a better comparison, the results obtained with 900 kHz apparatus under the same conditions are also presented in Figures 4.2 and 4.3. The power setting at 900 kHz was set at position 3 which delivered 33 acoustic watts inside the sonicated vessel.

The pH of the solution was monitored by a pH meter after each sonication time. Figure 4.4 shows the change of pH against the sonication time.

4.4 Discussion

4.4.1 Decomposition of chlorobenzene

Sonication of dilute aqueous solutions of chlorobenzene led to the following observations: (a) the concentration of chloride anion is increased by increasing the sonication time (Figures 4.2), (b) the intensity of a yellow color produced by sonication is increased by increasing the sonication time; it became slightly cloudy after prolonged sonication, (c) the pH of the sonicated solution decreased rapidly except for 20 kHz with the small horn (Figure 4.4) and (d) the HPLC results indicated a corresponding rapid decrease in the concentration of chlorobenzene. These observations confirmed the decomposition of chlorobenzene and also indicated the probable formation of HCl from sono-dissociation of chlorobenzene.

There are three possible places for this decomposition process: (a)

Figure 4.4: pH of the sonicated solution vs sonication time.
● 20 kHz with small horn,   ◆ 20 kHz with X-large horn,
■ 900 kHz.

inside the bubble during the collapse of the cavity, (b) in the solvent layer surrounding the bubble and (c) in the bulk solution phase. In cases (a) and (b), the pyrolysis and radical reactions occurred simultaneously and in the case of (c) free radical reactions (derived from the dissociation of water) are likely to predominate.

It can be suggested by the following observations that the main decomposition reaction occurred as a second reaction inside the bulk of solution. This can be done through the reaction of chlorobenzene with OH radical derived from the dissociation of water inside the bubble during the collapse of the cavity. The degradation rate was increased by decreasing the acoustic intensity through different tip sizes at constant power. Owing to the low concentration of solute and its lower vapour pressures than water; they are therefore unable to diffuse into the cavity and are not affected by the critical conditions generated by the cavitation collapse. Instead, neat chlorobenzene itself undergoes sonochemical reactions. Peeter Kruus et al have done some sonications on the pure substituted benzenes for the formation of polymers. They suggested a free-radical mechanism for polymerization which initiated through a thermal decomposition in a cavitation bubble [Kruus, 1983; Diedrich, 1972].

One of the main products of this decomposition is a yellow compound which is not identified yet. With increasing the time of sonication, the concentration of this unknown compound was increased. In short time

sonication, the solution was a clear yellow solution, but after longer times it became slightly cloudy. In case of long time sonication, an orange precipitate appeared to settle out of the solution after a day. It seems that the solution can be saturated by the unknown compound after a short time of sonication.

The H-NMR spectrum of the solution of chlorobenzene in deuterium oxide before (Figure 4.5) and after sonication (Figure 4.6) was different. Before sonication, there was a small triplet peak above 7 ppm which belongs to the chlorobenzene. In the spectrum after sonication, there was a strong doublet peak above 7 ppm and also a small peak around 10 ppm. This means that chlorobenzene had decomposed and produced another aromatic compound. According to the spectrum, the products could be either 1,2,3,5 tetrachlorobenzene or a mixture of benzene and 1,3,5 trichlorobenzene.

4.4.2 Intensity effect

At the same overall power, the rate of decomposition was greater with the X-large tip than with the small tip at 20 kHz irradiation. This means that the decomposition rate was more efficient at low intensity than at high intensity at the same power.

According to Figures 4.2 and 4.3, it is possible to estimate a curve for a horn with tip area the same size as 900 kHz (21 cm^2) by assuming a linear relationship between the rate and the tip sizes.

Figure 4.5: *The ^1H -NMR spectrum of the solution of chlorobenzene in deuterium oxide before sonication.*

Figure 4.6: The ^1H -NMR spectrum of the solution of chlorobenzene in deuterium oxide after sonication.

4.4.3 Frequency effect

There are a few reports in the literature about the ultrasonic degradation of organic compounds. Some of them describe the effect of frequency on the decomposition rate of organic compounds. J. Berlan et al [1994] recently studied the oxidative degradation of phenol in aqueous media using ultrasound. They used a Biosonic GW10 at 541 kHz apparatus, fitted with a submersible 12 cm horn, and a Sonic & Material Vibracel 600 at 20 kHz apparatus fitted with an immersible 12 mm horn. They observed a frequency effect, as the phenol remains almost unchanged at 20 kHz after 2 hours, but is totally degraded after 100 min at 541 kHz. These results are consistent with the previously reported results [Lur'e, 1962; Chen, 1971; Petrier, 1993]. Our results in general show that this difference is not only related to the frequency effect, but that the surface area of sonicator (12 cm and 12 mm horn) is also important and should be considered.

In sono-dissociation of chlorobenzene, comparison of the results at two different frequencies under exactly the same conditions shows that the real effect of frequency on this decomposition is about 1.5 - 2 times greater with 900 kHz than with 20 kHz.

4.5 Conclusion

Destruction of aromatic compounds needs extreme conditions, but ultrasound facilitates this degradation under mild conditions. This destruction

can be more efficient by increasing the surface area of irradiator and using high frequency.

CHAPTER 5

SONOCHEMICAL DISSOCIATION OF CARBON DISULFIDE

5.1 Introduction

In the literature, the uses of ultrasound in heterogeneous systems are divided into two groups: liquid-liquid and liquid-solid interactions. There is another class of reaction which is homogeneous before, but heterogeneous after sonication. The sonochemical reactions associated with metal carbonyls in an alkane as a solvent illustrate the change from homogeneity to heterogeneity by ultrasound. Grinstaff et al. [1992] found that the ultrasonic irradiation of iron pentacarbonyl ($\text{Fe}(\text{CO})_5$) under conditions that maximize the cavitation intensity (for example, Ar, low vapour pressures, low ambient temperatures) result in amorphous iron.

This amorphous iron powder is formed from the enormous heating and cooling rates generated during acoustic cavitation. The effective temperature reached during bubble collapse is about 5200 K with submicrosecond lifetime [Suslick, 1986]; the lifetime of these bubbles are also estimated to be less than one nsec [Barber, 1991]. It is thus expected that heating and cooling rates during cavitation collapse should be in the range of 10^9 - 10^{13} K s⁻¹. Acoustic cavitation might therefore provide a new method for formation of amorphous material which needs enormous rate of cooling.

This chapter reports the results of a study of the sonochemical decomposition of carbon disulfide. This system is homogeneous before, but heterogeneous after sonication. The variation of the rate of dissociation was studied as a function of ultrasonic frequency and power, horn tip area,

temperature, and the presence of gases.

5.2 Experimental procedure

The experimental apparatus have been described [Entezari, 1994]. The ultrasonic equipment used for 20 kHz was a Vibra-Cell VC375 ultrasonic processor with horns having tip area of 1.1 cm^2 (referred to as "small") and a special horn provided by Vibra-Cell with a tip area of 8.04 cm^2 ("X-large"). The 900 kHz apparatus was specially designed and constructed; it used the electrical supply obtained from Meinhardt Ultrasonics in Leipzig, Germany.

In this series of experiments, 50 mL of carbon disulfide was poured into a Rosette cell for direct sonication with 20 kHz by two different horns. The power was set at position 7, unless otherwise indicated; this delivers 49 W acoustic power into the solution by both horns at 298 K. The position of both horns was the same with respect to the Rosette cell. Unless otherwise indicated, the runs were done under a normal atmosphere with no gases bubbled through the solution. In the study of gas effects, 100 mL of carbon disulfide was sonicated inside a cell specially designed for gas studies.

After sonication, the solid phase (black particles) was separated from liquid phase (yellow solution) by a filter paper. The mass of black particles in a sample run with 100 mL under normal atmosphere for one hour was about 0.04 g (small horn). The black particles were collected from several runs. The yellow solution was also evaporated at room temperature and the remaining

solid phase collected. Both sample were sent for ESM (Electron Scan Microscopy), x-ray spectrum and element analysis.

Sonication of sample with a 50 kHz ultrasonic bath (Bransonic 1200) was done under a normal atmosphere for 4 hours. An Erlenmeyer containing 100 mL of sample was immersed into the ultrasonic bath with water as the coupling fluid.

Sonication with 900 kHz was also for a 100 mL samples under air, Ar, and He atmosphere. Owing to the interaction of carbon disulfide with RTV on the piezoceramic (Chapter 2), the sample was sonicated indirectly by immersing a container (125 mL Erlenmeyer) into the cell with water as the coupling fluid.

The rate of dissociation was followed by monitoring the intensity of colour by Uv-Visible at 379 nm (maximum absorbance, Figure 5.1) vs time using four or five data points. This rate can also be followed by the mass of black particles produced by sonication, but owing to the small amount of precipitate, the intensity of colour was preferred. During the rate determination, the temperature varied somewhat depending on the acoustic power. At low power, the temperature was constant to within $\pm 3^{\circ}\text{C}$ during a run, while at the highest power it could vary up to $\pm 7^{\circ}\text{C}$ when the temperature of the thermostat was set at zero degrees.

The effect of temperature on the dissociation of carbon disulfide was studied in the range of -50°C to $+10^{\circ}\text{C}$ using a dry ice-acetone bath. In this case the variation of temperature in during a run varied up to $\pm 12^{\circ}\text{C}$.

Figure 5.1: *The Uv-Visible spectrum of yellow solution produced by sonication of carbon disulfide.*

5.3 Results

5.3.1 Intensity dependence

The variation of the dissociation rate of carbon disulfide with two different tip sizes at 20 kHz is shown in Figure 5.2. It is evident that the rate of dissociation is larger with the small horn than X-large horn. It means that a higher intensity (44.5 W cm^2) is more effective than lower intensity (6.10 W cm^2) under the same power (49 W). This comparison was done under the same condition and the only variable was the size of the tip. The data in Figure 5.2 was obtained with power setting at position 7 (49 W), and the temperature of the system was set at zero degrees (ice bath).

Figure 5.3 shows the rate of dissociation with two different tip sizes under different power. This figure again indicates that the rate of dissociation is larger with the small horn at all power setting. In this range of power, the rate of dissociation of carbon disulfide is linear with X-large horn, but is not linear with small one; at the highest intensities, the reaction rate per unit power drops off.

The high intensity with the small horn causes a migration of a large fraction of the visible bubbles out of the solution. Many bubbles can also be seen close to the transducer tip. These must interfere with the introduction of ultrasound into the liquid. This is a possible explanation of the "saturation" of the sonochemical effect at higher intensities noted in Figure 5.3 .

Figure 5.2: Time variation of sono-dissociation of carbon disulfide using 20 kHz irradiation with two different tip sizes. ♦ Sonication by small horn (1.10cm^2); ■ sonication by X-large horn (8.04cm^2). The temperature was set at 0°C by an ice bath; the power was fixed at position 6 (42 W in case of water at room temperature). Corrections for loss of carbon disulfide during sonication and in filtration has been considered. The error bars show the standard deviation of the average of 3 independent runs.

Figure 5.3: Variation of sono-dissociation of carbon disulfide vs power at 0°C with two different horns. ♦ Sonication by small horn; ■ sonication by X-large horn at different power positions of 3, 5, 7, 9, 10 (21, 35, 49, 64 and 71 W respectively in case of water at room temperature). The data are the average of 3 runs. An estimated curve — is shown for the case of 20 kHz with tip area the same as 900 kHz (21 cm²).

5.3.2 Temperature dependence

The sonochemical dissociation of carbon disulfide was measured in a range of low temperatures ($-50 \approx +10^{\circ}\text{C}$) to prevent excessive evaporation. Figure 5.4 shows the rate of dissociation with respect to temperature for the two different tip sizes. There was some loss of carbon disulfide during sonication and filtration for separating the solid phase from the yellow solution, but a correction for this loss of volume was made on Figure 5.4. This figure again shows that in this range of temperature, the rate is greater with the small horn than with the X-large one and also the rate change of dissociation against temperature is greater with the small horn than with the X-large one.

5.3.3 Gas dependence

The effect of different gases (Ar, H_2 , Air, He, O_2 , CO_2) was studied on the sono-dissociation of carbon disulfide (Table 5.1). Each gas was bubbled through liquid carbon disulfide for 30 minutes before sonication and also the 30 minutes of sonication at a lower bubbling rate. These experiments were done under the same conditions except the nature of the gas. The noise from the cavitation process was louder, and the filtration for separation of the two phases was longer for helium and hydrogen than for the other gases. These observations showed that the cavitation collapse was more intense with hydrogen and helium than the other gases.

Figure 5.4: Variation with temperature of sono-dissociation of carbon disulfide using 20 kHz irradiation with two different tip sizes. $\blacklozenge$ Sonication by small horn; $\blacksquare$ sonication by the X-large horn at power position 7 (49 W in the case of water at room temperature). The data are the average of 3 runs.

5.4 Discussion

5.4.1 Dissociation of carbon disulfide

The dissociation of carbon disulfide by sonication might be explained by the collapse of the cavity which produces very high temperature (roughly 5000°C), pressure (roughly 500 atm), and cooling rates above 10^9 K/sec [Suslick, 1986]. Another important factor could be low heat conductivity of carbon disulfide vapour (Table 5.1). Under this critical conditions the C-S bond is broken and produce carbon and sulfur. Due to this process, the homogeneous carbon disulfide liquid is converted to the heterogeneous solution with a very fine black particles and a yellowish solution.

5.4.2 The x-ray spectrum

The x-ray spectrum of the fine black particles showed that a signal for sulfur (monoclinic, ≈ 24.5 Degree), another signal for titanium (≈ 40 Degree), which belonged to the ultrasonic probe, and a wide signal for amorphous carbon (Figure 5.5). The black sample was analyzed for carbon, and was found to contain 24.74% carbon, which was in an amorphous form. There is only 16% of carbon by mass in carbon disulfide.

The signal for monoclinic sulfur from the black particles could be related to the sulfur dissolved in the carbon disulfide (a yellow solution produced by sonication) which was adsorbed by the carbon. It should be noted that this sample was sent for x-ray analysis without washing.

The x-ray spectrum of the evaporated solution (yellow solution) also indicated a presence of much more monoclinic sulfur together with an amorphous phase (Figure 5.5) which might be related to the small black particles passed through the filter paper.

ESM also confirmed the presence of sulfur and carbon in the two phases after sonication.

Another sample of the solid was prepared by sonication of carbon disulfide in a dry ice-acetone bath at -50°C . The black particles at this temperature attached to each other more and were roughly separated by decantation. They were put in chloroform and mixed. The black particles stayed in the chloroform phase, which was then placed on a washglass and allowed to evaporate. An x-ray analyses of the remained black particles did not show any signal for sulfur (Figure 5.5). The most probably adsorbed sulfur had thus been washed from the black particles by chloroform. This spectrum presented a very large and broad peak for amorphous carbon.

5.4.3 Effect of intensity

Figure 5.2 shows the effect of tip size on the dissociation rate with 20 kHz irradiation. At the same overall power, the rate is greater with the small tip, that is, with the higher intensity. This result is opposite to the results for to the sonication of potassium iodide solution with different horn sizes (Entezari, submitted 1994). Figures 5.3 and 5.4 show this effect to be generally valid.

Figure 5.5: X-ray spectrum of the products produced by sonication of carbon disulfide. (a) black particles without washing, (b) solid phase produced by evaporation of yellow solution and (c) black particles washed by chloroform. The sharp peaks in curve (b) are from the special sample holder.

This different behaviour might be related to the different cavitation process. In the case of carbon disulfide, the dissociation should be most probably happened inside the bubble as a first reaction. In potassium iodide solution, the oxidation process is a secondary reaction which would occur in the liquid, following the dissociation of water inside the bubble.

In general, an increase in intensity will provide an increase in the acoustic amplitude. Since the collapse time, the temperature, and the pressure on collapse are dependent on the acoustic amplitude, the bubble collapse will be more violent at higher acoustic amplitudes. This will cause an increase in the sonochemical effects.

According to the Figure 5.3, it is possible to estimate a curve for a horn with tip area the same size as 900 kHz (21 cm^2) by assuming a linear relationship between the rate and the tip sizes. The slope of the rate vs power graph for this case is about one fifth of the small horn (1.1 cm^2). At a power of 20 W, the rate of reaction is expected to be very small.

Sonication of carbon disulfide with 900 kHz for an hour produced no visually observable change. The GC-MS chromatogram also showed no change before and after sonication. Due to the indirect sonication, the power reached inside the reaction place was about 20 W. Another run with higher intensity ($\approx 60 \text{ W}$) for 15 minutes also produced no noticeable change.

Sonication of carbon disulfide in a 50 kHz ultrasonic bath for four hours also led to the conclusion that there was no apparent change due to sonication.

This may be related to its very low intensity. The rate of oxidation of potassium iodide in the ultrasonic bath sonicator was very slow; sonication of 50 mL of potassium iodide for one hour led to the formation of 0.6 μmol iodine, about 2% of the rate of oxidation with the 900 kHz apparatus.

The experiments with the 50 kHz bath are of importance, as sonication in carbon disulfide is a common method of separating trapped impurities from filters used to evaluate air quality. Any formation of carbon from the solvent would mean faulty analysis of air particulate level.

5.4.4 Effect of temperature

Figure 5.4 shows the effect of temperature on the rate of dissociation of carbon disulfide. In this range of temperature, the rate with the small horn is greater than that with the X-large horn. With increasing the temperature the rate of dissociation is decreased for both horns. With an increase in temperature, the vapour pressure inside the bubble is increased, and hence the collapse of the cavity is cushioned, leading to more moderate conditions.

5.4.5 Effect of gas

The presence of gas in the bubble has dramatic affects on the cavitation collapse. There are several parameters of gases that can affect sonochemical reactivities. The heat capacity ratio γ ($=C_p/C_v$) which affects the final temperature produced by a gas during compression. Monatomic gases

with highest heat capacity ratio give the highest temperature; polyatomic gases with lower γ give lower temperature. Another parameter that affects cavitation collapse is the thermal conductivity of the gas. The gas with the higher thermal conductivity reduces the collapse intensity and lowers the final temperature. According to the hot spot theory, a gas with high γ and low heat conductivity has more efficiency on the sonochemical activities. The solubility of the gas in the liquid used is also an important aspect.

The results summarized in table 5.1 show the order of dissociation of carbon disulfide as $\text{He} > \text{H}_2 > \text{Air} > \text{Ar} > \text{O}_2 > \text{CO}_2$. According to the table 1, it seems that the solubility is a predominant factor and determines the approximate order of the dissociation rate. This order was confirmed quantitatively by the intensity of color as well as by the mass of black particle produced by ultrasound. More evidence for this order can be qualitatively obtained based on the intensity of cavitation noise, for example, the intensity of cavitation noise was much harsher under hydrogen and helium than other experienced gases.

Air, H_2 , and O_2 may have a reaction with intermediates species produced by ultrasound, so that for an explanation attention should be given to the He and Ar results. According to the hot spot theory, the sonochemical activity should be higher under Ar [Grinstaff, 1992] than He due to the lower heat conductivity of Ar than He. Our results showed an opposite behaviour. This situation may be due to consideration of other properties of the gases, such as

Table 5.1: Variation of sono-dissociation of carbon disulfide by 20 kHz ultrasound with different gases. Heat conductivity (H.C.) is in unit of $\text{Cal}/(\text{sec})(\text{cm}^2)(^\circ\text{C}/\text{cm}) \times 10^6$ at 4.4°C , γ is heat capacity ratio at 25°C ; solubility of gases (S) at 298 ; absorbance (Abs.) of colored solution produced by ultrasound was measured at 379 nm after 30 minutes of sonication (Average of 3 runs).

Gas	H. C.	γ	$S(X_g/10^{-4})$	Abs.
Air	58.31	1.39	----	0.248 ± 0.012
Ar	40.09	1.67	4.9	0.199 ± 0.045
H ₂	417.39	1.40	1.6	0.297 ± 0.005
He	343.42	1.67	1.2	0.312 ± 0.018
O ₂	59.43	1.39	4.4	0.167 ± 0.016
CO ₂	35.62	1.29	32.8	0
CS ₂	16.53	1.22	----	-----

the solubility; such data are however not available.

5.5 Conclusion

The major contribution of this work is to present a new method for formation of amorphous carbon from sonochemical dissociation of carbon disulfide using a 20 kHz apparatus. This dissociation is more efficient under helium and hydrogen gas than air, argon or oxygen. There is however no observable change when sonication is carried out with 900 kHz under He, Ar and air, nor with a 50 kHz ultrasonic bath. This study also showed that the effect of tip size on this reaction is the reverse of that found in the oxidation of potassium iodide.

CHAPTER 6

SUMMARY AND CONCLUSIONS

6.1 Apparatus

The first major contribution of this study is the design and construction of a new apparatus which produces 900 kHz ultrasound through a flat transducer mounted at the bottom of a reaction vessel holding the solution. The power amplifier for this apparatus was obtained from Meinhardt Ultrasonics in Leipzig, Germany.

In order to improve the reproducibility of the results, we designed and made some devices which facilitated the repetition of experiments under identical conditions. For example, the position of the cell in the acoustic field was adjustable by a holder equipped with a micrometer. The temperature of the solution was controlled by a coiled glass tube inside the solution and circulating water outside the vessel. With a good control on the system, it was possible to have a reproducibility even to about 1% under some conditions. It is important to have good control on the system to get good reproducibility.

The behaviour of the solutions during sonication at 900 kHz differs markedly from that at 20 kHz. There is no cavitation noise at 900 kHz to be heard in the audible range; while at 20 kHz, this could be very harsh and irritating to the ears even with ear protection. This is one of the advantages of studying and utilizing sonochemistry at higher frequencies.

It is visually apparent that the cavitation bubbles are much smaller at high frequency (900 kHz) than at low frequency (20 kHz); fewer bubbles also migrated to the top of the solution and if we assume that each cavitation bubble

is a "mini reactor", we will lose more "mini reactors" with low frequency than with high frequency.

Sonication with 20 kHz is accompanied by contamination of the sonicated solution with small particles produced by an eroded horn. In contrast, direct sonication with the 900 kHz apparatus might have introduced some contamination of the sonicated solution owing to a RTV layer on the piezoceramic transducer. Sonication of carbon disulfide and aqueous solutions of chlorobenzene were done indirectly. In this case, there is no contamination, and about 70% of the acoustic power still enters the sonication cell.

6.2 Temperature

The second major contribution of this study is to note the effect of temperature on the sonochemical reactions which is different at different frequencies. In the case of 20 kHz, as the temperature of the solution is increased, the reaction rate generally decreases. The shape of the rate versus temperature relation is dependent on the acoustic power.

By contrast, in the case of 900 kHz, the reaction rate versus temperature can show a maximum. The position of this maximum is dependent on the power level. An increase in the power moves this maximum toward a lower temperature. The maximum may even disappear at powers higher than those available in our laboratory. The shape of the curves was explained by the ratio of partial pressures of dissolved gas and the vapour of the liquid. These results

also clarified some contradictory results in the literature.

6.3 Power and intensity

The variation of the rate with acoustic power at 20 kHz is not linear. At higher power, the reaction rate drops off from linearity; a clear cavitation threshold is not evident in sonication of potassium iodide. However, sonication of carbon disulfide shows a clear cavitation threshold at 20 kHz. At very high intensities, the application of more power may be counterproductive. There are so many large cavities under the tip that the contact between tip and liquid is poorer, and the acoustic energy is dissipated to a greater extent into heating the horn. However, the variation of the rate with acoustic power at 900 kHz is linear in the range available experimentally, and there is a clear cavitation threshold, at least for potassium iodide solution.

The third major contribution of this work is to study the effect of tip size on the reaction rate with 20 kHz irradiation. This effect is related to the type of reaction. For example, in the sonication of potassium iodide solutions and dilute solutions of chlorobenzene, at the same overall power, the rate is greatest with the largest tip, i.e. with the lowest intensity. In contrast, in the case of sonication of carbon disulfide, the effect of tip size is reversed.

Why with increasing the tip size at constant power (decreasing the intensity) do the rates of some reactions such as sonication of aqueous potassium iodide and dilute aqueous solution of chlorobenzene increase and

the rates of some other reactions such as sonication of carbon disulfide decrease? Giving a general answer to these questions requires the study of more different systems. According to the results, the reactions can be divided into two groups.

First, the reactions which occur in the interior of a collapsing bubble as a first reaction such as sono-dissociation of carbon disulfide. In this case the bubble collapse will be more violent at higher intensities (smaller tip size than larger one at same power). The second group is where a secondary reaction occurs in the liquid such as sonication of aqueous potassium iodide and aqueous dilute solution of chlorobenzene, following the dissociation of water inside the bubble. The iodide anion in aqueous solution can not participate inside the bubble owing to its non-volatility and therefore it must be oxidized outside the bubble.

Neat chlorobenzene itself undergoes sonochemical reactions. In this case, the concentration of solute is very low (≈ 200 ppm) and its vapour pressure is lower than that of water. Very little chlorobenzene will thus be present inside the bubble. Therefore secondary reactions in the aqueous media will likely dominate.

Intensity is a very important factor such that irradiation at two different intensities can give completely different results.

6.4 Gas

The nature of the gas present in the solution does affect the reaction rates. For example, in the case of aqueous potassium iodide solution, with 20 kHz irradiation, the order of the reaction rate is: argon > air > degassed, while with 900 kHz it is: air > degassed > argon. The order of dissociation of carbon disulfide with 20 kHz under different gases is: He > H₂ > Air > Ar > O₂ > CO₂. These differences in behaviour can be explained by the different properties of the gases (e.g. solubility, ratio of heat capacities, thermal conductivity) and the spatial and temporal behaviour of the cavitation bubbles at the two different frequencies.

6.5 Frequency

In our initial experiments, we found that with the newly designed 900 kHz apparatus the rate of oxidation of potassium iodide could be as much as 30 times greater than with 20 kHz. The conditions for both apparatuses were exactly the same, but there was an intrinsic difference in the surface area of ultrasonic irradiator. The surface area for 900 kHz was 21 cm² and for 20 kHz only 1.1 cm². This increase of rate is related to the frequency effect, but also to the surface area. The rate of oxidation with 900 kHz apparatus is estimated to be about 2 times greater than with 20 kHz.

In the case of dilute aqueous solution of chlorobenzene, the rate of decomposition with 900 kHz apparatus was much more than with 20 kHz. With

study of the tip size on this reaction, we estimated the rate of decomposition with a tip equal size to 900 kHz apparatus. Comparison of the results showed that the real frequency effect on this dissociation is ≈ 2 times greater with 900 kHz than 20 kHz. These results are of significance for attempts to eliminate organohalides from water with ultrasound. It is obvious that the use of a higher frequency is more promising.

The fourth major contribution of this work is to present a new method for formation of amorphous carbon from sonochemical dissociation of carbon disulfide using a 20 kHz apparatus. The results of a study of the tip size on this dissociation suggest that a noticeable reaction should occur with the 900 kHz apparatus. There was however no observable change when sonication is carried out with 900 kHz. This difference must be due solely to the effect of frequency.

6.6 Summary

The major contributions of this study are:

- 1) The design and construction a new 900 kHz apparatus
- 2) Finding different behaviours with respect to temperature at two different frequencies
- 3) Discovery of the effect of tip size on the reactions at 20 kHz
- 4) Discovery that high frequency is more effective for eliminating organohalides (chlorobenzene) from water than low frequency.
- 5) Development of a new method for formation of amorphous carbon from sonochemical dissociation of carbon disulfide

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APPENDIX

ULTRASONIC HYDRATION OF UO_2

Note: This chapter was chosen as an appendix due to two reasons. First, there were no significant changes in the reaction with sonication as compared to other mechanical methods. Second, a focussed ultrasonic apparatus was used for sonication and it had an acoustic field different from the others.

A-1 Introduction

The use of ultrasound in heterogeneous systems is in the literature divided into two groups: liquid-liquid and liquid-solid interactions. In immiscible liquids (liquid-liquid) ultrasound can generate extremely fine emulsions which result in the dramatic increase in the interfacial area between the liquids. This process facilitates the reaction between species dissolved in the different liquids. In solid-liquid interaction, there are two types of reaction. In one reaction, the solid plays the part of catalyst; in another it acts as a reagent and is consumed in the process.

Historically, Renaud [1950] was the first to use ultrasound in heterogeneous liquid-solid reactions. He prepared some organometallic compounds with metals such as Al, Li, and Mg. Microjet and shockwave are thought to be responsible for localized erosion and also the sonochemical effects on heterogeneous reactions. For example, when liquid-powder slurries are irradiated by ultrasonic waves, the cavities and the shock waves which are produced can accelerate solid particles to high velocities. The resultant interparticle collisions are capable of inducing dramatic changes in surface

morphology, composition, and reactivity. Luche and Damiano [1980] reported a direct formation of alkyl and aryl lithiums by reaction of organic halides with lithium wire. This ultrasonic activation of stoichiometric heterogeneous reactions was carried out with an ordinary ultrasonic cleaner which gave excellent yields (61-95%). Boudjouk [1981] reported the synthesis of novel cyclic compounds and the production of new reactive intermediates with the reactions of difunctional organosilanes and lithium. This reaction has done with lithium dispersions in tetrahydrofuran with reaction times about 20 minutes and a yield of about 85%.

The synthetic utility of lithium, magnesium, and other reactive metals in heterogeneous synthetic organic reactions is showed by the intense investigation into the activation of these metals by ultrasound. In this kind of synthesis, as a general, ultrasonic irradiation increases reaction rates, increases product yields, and decreases induction periods. Ultrasonic irradiation also allows reactions to proceed at lower temperatures, reducing side reactions and achieving better reaction control.

An increase in the efficiency of heterogeneous reactions with ultrasound can be due to a number of different causes such as: reduction of particle size, thereby increasing the reactive surface area [Lindley, 1986]; intense mixing which improves the mass transport [Repic, 1982]; removal of passivating surface coatings which cleans and activates the surface [Suslick, 1989c]. The main mechanisms responsible for the cleaning process in an ultrasonic field are

cavitation, acoustic streaming and the formation of a pressure gradient across the particles [Kashkoush, 1990, 1992, Geers, 1991]. The removal of contamination was studied by high speed photography [Rozenburg, 1960]. This study proposed two mechanisms for removal of contamination films. The first one was the partial tearing of a film from the surface by the collapse of the bubble; the second was the penetration of energetic small bubbles into all pores and gaps between the contamination layer from the surface.

A.2 Experimental Procedures

A.2.1 Types of apparatus

Two frequencies of ultrasound were used in these experiments, 20 and 850 kHz. The 20 kHz ultrasonic wave was produced by a Bransonic Cell Disrupter model 350. The Disrupter was coupled to a Bransonic 102 converter and a titanium horn which transmitted the ultrasound directly to the sample solution. The reaction vessels used were two sizes of bumpy bottom vessels, or a 250 mL beaker. The temperature was controlled by a circulating water thermostat.

An Ultraschalltechnik apparatus was used for producing 850 kHz ultrasonic waves. The solutions were irradiated indirectly through the concave metal piece at the bottom of the system (see Figure 1). The reaction vessels for this apparatus were the same as for the 20 kHz apparatus, but without the bumpy bottom.

Figure A.1: *The 850 kHz apparatus with a concave transducer.*

A.2.2 Intensity calibration

It is important to periodically check the acoustic power delivered to the liquid. This was easily done in the case of the 20 kHz apparatus by immersing the horn tip in a known amount of water in a Dewar flask and noting the rate of temperature increase on irradiation.

In the case of 850 kHz ultrasound, it is more difficult to obtain a measure of the acoustic power delivered to the solution as there is no direct coupling. The conic shape of the ultrasonic wave produced in this system means that the acoustic power is quite different at different points in the solution. A chemical dosimeter must thus be used for this apparatus.

There are several chemical dosimeters: the formation of hydrogen peroxide followed by the oxidation of I^- to I_2 as measured by spectrophotometry, the use of the stable free radical, diphenylpicrylhydrazyl, as a radical trap in non-aqueous sonochemistry, and the decomposition of iron pentacarbonyl.

A.2.3 Hydration of uranium trioxide

Uranium trioxide (UO_3) powder from Cameco was sieved by a mechanical shaker. The hydration was carried out by three methods:

- a) Sonication at 20 kHz with and without stirring
- b) Sonication at 850 kHz with stirring
- c) Agitation by stirring without ultrasound

A.2.4 Experiments at 850 kHz

In a typical experiment, 25.0000 ± 0.0002 g of UO_3 of a specific size fraction was weighed and put into a 50°C oven for one night. One hundred millilitres of distilled water was poured into a vessel designed specifically for 850 kHz ultrasonication (see Figure A.1). The vessel was then immersed in the ultrasound-bath and allowed to reach thermal equilibrium. Uranium trioxide was added into the water and the system was irradiated with ultrasound while agitated by a stirrer for a period of time. The stirrer was used because the ultrasound (850 kHz) could not keep the uranium oxide in suspension.

After ultrasonic irradiation, the suspension was transferred to a 250 mL beaker and the orange colored solids were separated from the yellow colored ones by decantation. After filtering, both of them were put into the oven at 50°C overnight. The weight of each sample was determined after drying in this manner.

A.2.5 Experiments at 20 kHz

The conditions for 20 kHz were the same as 850 kHz, but the shape of the vessels were different and also the systems were sonicated in presence and absence of agitation. In the absence of stirring, the streaming could usually keep most of the powder in suspension. The acoustic energy forces the fluid and particles down towards the centre of the bottom of the vessel, where they are deflected upwards along the sides.

A.2.6 Experiments without ultrasound

Experiments were also done using a beaker (250 mL) as a reaction vessel. The suspension was mixed with different kinds of stirrers without any ultrasonic irradiation.

It was possible to control the temperature in the 20 kHz experiments to within 2 ° C of the starting temperature (after an initial 5 minute period) and in the 850 kHz experiments to within 2 °C from the initial time.

A.3 Factors affecting the rate of hydration

A.3.1 Effect of temperature

This series of experiments were done by 20 kHz without stirring at 17.6 W/cm². A sample of 25.0000 gr with mesh size of -60+80 was suspended in 135 mL water inside a bumpy bottom vessel.

Table A.1 shows the rate of hydration at different temperatures. It is clear that with increasing temperature the rate of hydration is increased.

Table A.1: *Rate of hydration at different temperatures*

Temp./°C	Rate of Hydration/ (g/min)
22.8	0.011
31.7	0.020
43.7	0.045
62.0	0.077

From the plot of $\ln(\text{rate})$ versus $1/T$, an experimental enthalpy of activation can be calculated as 43 kJ/mole. The plot is not linear, especially at higher temperature. The actual enthalpy of activation for the hydration process is therefore probably somewhat higher than this. Using only the three lower temperature points, the calculated value is 58 kJ/mole. The non-linearity at higher temperature may be due to the reaction becoming diffusion limited i.e. diffusion of the water through the previously hydrated outer layers of the solid particles.

A.3.2 Effect of shape of cell

Three different vessels were used under the same conditions (20 kHz, 50°C, 25 g, -60+80 mesh UO_3 , 135 mL water). Referring to Table A.2, the rate of hydration is significantly affected by the shape of the vessel used. The small bumpy bottomed vessel produced the largest rate of hydration.

Table A.2: *Effect of type of vessel on rate of hydration*

Type of vessel	Rate of Hydration (g/min)
Large Bumpy	0.077
Small Bumpy	0.134
Rosette Cell	0.048

It should be noted that these changes of hydration rate are not only

related to the shape of the vessel, because a few parameters (especially agitation) were not constant. There was little motion of the UO_3 particles through the arms of the rosette cell, explaining the low rate in this cell.

A.3.3 Effect of UO_3 mesh size

Figure A.2 shows the relationship between the mass of hydrated product and starting UO_3 particle size. The conditions for this series of experiment were the same as above. It was expected that the lower size fraction of the UO_3 would yield more hydrated material due to its higher specific surface area.

A.3.4 Effect of stirring

The effect of the presence of a magnetic stirrer on the rate of hydration by 20 kHz ultrasound was investigated. A magnetic stirrer in a plastic bag was placed in the bath beneath the vessel (a 150 mL beaker). The rate of hydration with stirring only was 0.027 g/min, while with a combination of stirring and sonication, the rate was higher (0.067 g/min).

A.3.5 Effect of power

With stirring, 125 mL of water with 25 g of UO_3 was irradiated by 20 kHz ultrasound at different intensities. A 150 mL beaker was used as a vessel. Table A.3 summarizes the results and shows that increasing the power increases the rate of hydration.

Figure A.2: The effect of particle size on the hydration of UO_3 .

Table A.3: Effect of power level on the rate of hydration

Power (W)	Rate (g/min)
60	0.064
78	0.095
87	0.105

A.3.6 Effect of hydrogen gas

Hydrogen gas was passed through a slurry of UO_3 in water during sonication. The product was similar to that obtained without hydrogen gas present, i.e. a yellow solid. There was no evidence of any chemical reduction having taken place. The quantity of hydrated material produced, however, was much lower with the hydrogen gas present, presumably due to the effect of the gas bubbles on transient cavitation.

A.4 Sonication in Organic Solvents

Two organic solvents were used, propanol and toluene. The reaction conditions used for both of them were the same. After sonication for a period of 60 minutes a small amount of hydrated product was produced in both solvents. The products were completely yellow, whereas in water medium the hydrated product had a greenish tinge.

The reason for having any hydrated product in propanol may be related to the OH group of the alcohol or the existence of water as an impurity. It

appeared that the "hydrated" material from sonication in propanol was much finer than that from water, since the former could not be trapped on a filter paper.

The reason for hydration in toluene must have been related to water as an impurity. Separation of the "hydrated" material was easily accomplished, indicating a coarser material.

A.5 Frequency and agitation

The kinetics of hydration using 20 kHz and 850 kHz ultrasound were measured. The kinetics were also measured without ultrasound, but using a magnetic stirrer (in the 20 kHz experiments) or a propeller-like agitator (in the 850 kHz experiments) for agitation. Figure A.3 shows the amount of hydrated material versus time under the same conditions of temperature, volume and UO_3 mesh size, but under different sonication or stirring conditions. It should be noted that a large magnet (almost the diameter of the beaker) was used for stirring in the 20 kHz experiments.

According to Figure A.3, the rate of hydration is greatest using magnetic stirring and no ultrasound. This may be related to the effectiveness of the stirring method at maintaining a good suspension, but also possibly due to changes in particle size during the mixing of the system. In other words, the UO_3 prills may be pulverized between the magnet and the beaker walls. However, a direct comparison can not be made in this case, since the

Figure A.3: Effect of ultrasonic frequency and stirring on the hydration of UO_3 .
 ♦ Stirring only, ♦ 850 kHz & stirring, ○ stirring only in 850 kHz cell, + 20 kHz (self-stirring).

experiments involving stirring without ultrasound were performed in a beaker, whereas those involving ultrasound were performed in the bumpy bottomed vessel.

The rate of hydration measured at 20 kHz is greater than at 850 kHz. This may be explained by a greater ultrasonic power or better mixing conditions at 20 kHz compared to 850 kHz.

Experiments were performed using a small magnet for agitation. This magnet was just large enough to keep the UO_3 in suspension. According to the result, the rate of hydration is greater in the case of ultrasound plus stirring than with only stirring, as expected.

A surprising thing was observed regarding the color of hydrated form of the UO_3 . In the presence of ultrasound, the color had a slight greenish tinge, whereas without ultrasound, the product was a definite yellow. One possibility was that the greenish color was due to titanium particles from the tip of ultrasonic horn immersed into the suspension. This was checked by SEM/EDS spectrometry. No titanium was observed in any of the samples tested.

Another idea was that the color difference was related to the amount of water of hydration. However, no difference in weight loss values at 270°C between the greenish and yellow samples could be observed.

An attempt was made to measure the percent water in samples by measuring the EDS oxygen peak intensity relative to that in UO_3 . Analysis of several greenish and yellow samples gave the following results:

Hydrated (yellow) $20.4 \pm 2.2 \%O$

Hydrated (green) $22.7 \pm 2.2 \%O$

Thus, there is a possibility that the application of ultrasound results in a slightly higher amount of hydration, and a material which has a slightly different colour.

A.6 Factors affecting the size distribution of the unhydrated UO_3

A.6.1 Temperature

The Scanning Electron Microscope was used to measure the particle sizes of the remaining orange material (presumably unhydrated UO_3) after sonication at different temperatures. Table A.4 presents the results in terms of the average projected particle area i.e. the area of the "shadow" projected by the particle. At least 400 particles were measured in each sample. This analysis was not possible for the hydrated material, since it was impossible to prepare the sample as a one-particle thick layer.

Table A.4: Particle sizes after sonicating at different temperatures

Temperature/ $^{\circ}C$	No. of Particles Counted	Mean Area/ mm^2
62	435	0.0257
43	480	0.0307
24	451	0.0252

Note: The starting UO_3 mesh size was -60+80.

There is apparently little correlation of the temperature with the resultant particle size of the unhydrated UO_3 .

A.6.2 Initial particle size

Several runs were done using UO_3 of different mesh size, and the standard run conditions listed earlier. Referring to Table A.5, the effect of sonication on the unhydrated UO_3 appears to have a greater effect on the larger size fraction. This may indicate that the ultrasound itself can only comminute the particles to a certain extent. Further comminution may require other forces (e.g. hydrolysis).

Table A.5: *Unhydrated particle areas before and after sonication*

Mesh Size	Mean Area/mm ² Before Sonication	Mean Area/mm ² After Sonication
(-170/+325)	0.0055	0.0059
(-80/+115)	0.0216	0.0224
(-60/+80)	0.0761	0.0529

A.6.3 Shape of cell

The mean unhydrated particle sizes obtained from sonication in different vessels are presented in Table A.6. First, the type of vessel used obviously affects the size distribution of the material. The small bumpy bottomed cell caused the greatest amount of comminution. This was not surprising, since the

material was observed to be in good suspension when using this cell. A somewhat surprising result is that the particle size using ultrasound and stirring was larger than that using stirring alone. Once again, however, this particle size is of the unhydrated material.

Table A.6. *Effect of type of cell used on particle size*

Type of Cell	Mean Area/mm ²
Rosette	0.0248 (U)
Small Bumpy	0.0109 (U)
Beaker 150 mL	0.0207 (U+S)
Beaker 150 mL	0.0178 (S)

Note: U = ultrasound, S = stirring

Note: -60+80 mesh size UO₃ was used

A.6.4 Sonication in organic solvents

The mean particle areas after sonication of UO₃ in toluene and in propanol are presented in Table A.7. Note that the original particle area was 0.0216 mm², and that sonication in water did not change the particle size of the unhydrated material appreciably (see Table A.5). The organic solvents, especially toluene, had a large effect on the particle size.

Table A.7: Particle sizes after sonication in organic solvents

Solvent	Mean Area/mm ²
Toluene	0.0083
Propanol	0.0113

Note: -80+115 mesh size UO_3 was used.

A.7 Conclusion

The effects of ultrasound on the hydration of UO_3 are considered by measuring the rate of hydration under different conditions of ultrasonic frequency, ultrasonic power and temperature. Also considered are the type of vessel, the mesh size of the UO_3 , and the type of agitation used.

In general, use of 20 kHz ultrasound resulted in faster hydration than use of 850 kHz. Higher ultrasonic power led to a faster hydration rate. Higher temperature also resulted in faster hydration. An experimental activation enthalpy of 58 kJ/mole was calculated. The shape of the sonication vessel was found to be important. Sonication in organic solvents produced very fine material. Addition of hydrogen gas during sonication in water did not produce any lower oxides of uranium.

VITA

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He received a Bachelor of Science in Chemistry from Mashhad University in 1985 and a M. Sc. in Chemistry from Mazandaran University in 1988. He did his research with Dr. F. Milani-nejad studying the de-icing properties of Asphalt.

He came to Ottawa on May 4, 1990. He entered Carleton University and joined the research group of Professor Peeter Kruus in January 1991. The author has spent the last four years studying the Effect of Frequency on Sonochemical Reactions.

Currently, he has the following:

Entezari, M.H. and Kruus, P. **Ultrasonics Sonochemistry 1994**, The Effect of Frequency on Sonochemical Reactions I: Oxidation of Iodide, 1, 2, S75.

Entezari, M.H. and Kruus, P. **Ultrasonics Sonochemistry 1995**, The Effect of Frequency on Sonochemical Reactions II: Temperature and Intensity Effects, accepted.

Entezari, M.H.; Kruus, P. and Otson R. **J. Am. Chem. Soc.**, The Effect of Frequency on Sonochemical Reactions III: Dissociation of Carbon Disulfide, submitted.

Entezari, M.H.; Kruus, P. and Otson R. **J. Phys. Chem.**, The Effect of Frequency on Sonochemical Reactions IV: Dissociation of Chlorobenzene in Dilute Aqueous Solution, plan to submit.

Some of this work has presented in:

76th Canadian Society for Chemistry Conference and Exhibition, Sherbrook, May 30, 1993.

Suslick's group at University of Illinois at Urbana-Champaign, U.S.A., January 1993.

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