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The Bubble's Burst: Sonochemistry and Free Radicals

by

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Abbreviations

ESR	Electron spin resonance
DMPO	5,5-dimethyl-1-pyrroline-*N*-oxide
MME	Methacrylate
TBD	Thymine base damage
TMPO	3,3,5,5-tetramethylpyrroline-*N*-oxide

Outline

i. Abstract

Sonochemistry is the study of chemical reactions that are initiated by treating a solution with high frequency ultrasound. These sound waves initiate the formation, and collapse of small cavities in solutions which produces thermal energy and, can leads to the production of free radicals. Sonochemistry has many applications. This unique field ofchemistry has been applied in small scale industrial synthesis, the purification of waste water, and as a tool for medical science. The unique chemical and biochemical reactions in sonochemistry are the focus of this review.

1 Introduction to sonochemistry

Sound surrounds us in our everyday lives. From the coo of a baby to the roar of jet liner, this almost ubiquitous force is constantly at work around us. As organisms, this makes hearing central to sensing events in our environment. Transmitted by vibrating particles, sound can pass though diverse mediums such as air or steel. While constructive in nature, such as a conversation, sound energy can also do harm. Acoustic energy far beyond what the human ear can pick up has the ability to initiate chemical reactions. This is the subject of sonochemistry.

Imagine a small vessel filled with water at rest. Water molecules freely move and pass one anther. Now, imagine this same vessel under the influence of ultrasonic energy. Sound waves cause compression and relaxation, leading to the formation of bubbles or cavities [1]. These cavities can be filled with water vapor, some other dissolved gas, or simply be a void. Cavitation can continue indefinitely, called stable cavitation, or result in collapse of the cavity, referred to as transient cavitation [1, 2]. After its initial formation, a bubble will grow in size with each wave of acoustic energy it absorbs. If the amount of input energy it increased, the bubble's size will increase until a critical radius is met. This causes the cavity to collapse and generates an enormous amount of internal energy. According to the first law of thermodynamics, if no heat is added during sonochemical experiments, it process is said to be adiabatic, or the change in internal energy is due only to work exerted by the sound energy. Therefore we can apply a variant of the ideal gas law ($P\Delta V + V\Delta P = nR\Delta T$) and the temperature of the system can be calculated. Calculations have shown that the temperature inside the collapsed bubble can reach upwards of 3000 K. The temperature also depend on a value called specific heat, which is an empirically determined value for all gases. This makes the amount thermal energy released is strongly dependent on the gas inside the bubble [3]. With such a local abundance of thermal energy, chemical reactions are bound to occur. High release of thermal energy leads to bond breakage and hence free radicals are formed [1]. These radicals can then diffuse into the solution and become involved in other chemical reactions. It is because of the formation of these radicals that ultrasound energy has important medical, biological and environmental applications [1, 4]. Chemical aspects important to each will be the focus of this review.

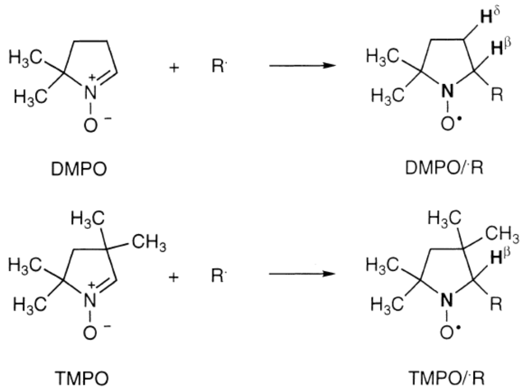

Figure 2.1: Reactions of 5,5-Dimethyl-1-pyrroline-Noxide (DMPO), and 3,3,5,5-tetramethylpyrroline-N-oxide (TMPO) spin **traps with free radicals [5].**

2 Detection of sonochemistry events

It is essential during the study of any chemical process to be able to measure it. The lifetime of free radicals can be short lived, which makes direct measurement a difficult task. During sonochemical experiments their detection is carried out by electromagnetic spin resonance, or ESR. In ESR a molecule referred to as a spin trap reacts with radicals to create longer lived spin adducts, which ESR can measure. Common among these spin traps are 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) and 3,3,5,5-tetramethylpyrroline-*N*-oxide (TMPO), which both quickly react with free radicals for measurement by ESR (**Figure 2.1)** [5]. Measurement by ESR has allowed researchers to do numerous studies in sonochemistry. Much of what is known in this filed would be impossible without it. It also has allowed researchers to measure both qualitatively and quantitatively the type of radicals produced in solutions after sonication. One such experiment was the discovery that super oxide is readily produced in many solution saturated with oxygen [5]. Physical properties of solvents and solutes that can influence radical generation during experiments have also been determined [6].

3 Chemical reactions in sonochemistry

3.1 Factors influencing chemical reactions:

Many factors influence chemical reactions driven by sonochemistry. Paramount of these is the frequency of sound energy used [6]. Lower frequencies, usually in the server hundred kilohertz (kHz) range, produce sufficient thermal energy to break bonds. However, higher frequencies (in the mega Hertz rage) may be required for compounds produced during industrial applications [7]. Solvent properties can restrict cavity size because of varying electrostatic properties, while dissolved gases have effects on the temperatures and free radicals produced after transient cavity collapse [3]. Physical conditions, such as temperature and pressure, during ultrasound treatment also influence radical formation [8].

3.2 Industrial aspects:

Unwanted organic compounds are common byproducts from industrial processes which must be removed prior to their release into the environment. Work by Kimura and colleagues demonstrated how acetic acid, an industrial solvent, can be broken down or converted into other useful compounds by ultrasonic treatment. In the process outlined in **Figure 3.1**, sound waves generate free radical intermediates which, through a multi step process, quickly react to form gases (H_2, CO_2, and Methane) in a [6]. Moreover industrial polymers can be formed for

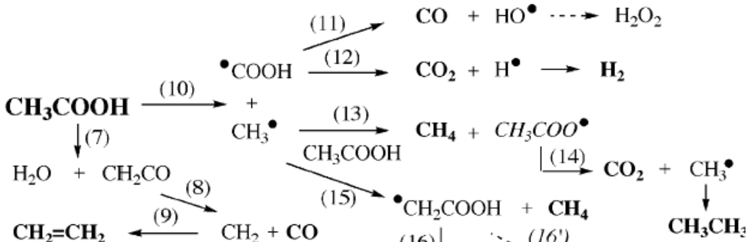

Figure 3.1: Schematic representation of acetic acid shock wave cleavage [6].

downstream applications. Ultrasonic treatment has shown promise in degrading the industrial pollutant *p*-chlorophenol [7]. Researchers attempted to use high frequency ultrasound (1.7 mHz) to initiate chemical degradation *via* free radical intermediates. The process was successful, producing in a single step chlorine and other non-organic compounds [7]. However the method does have shortcomings. Implementing such a process on an industrial level at this time is unlikely due the technological problem of delivering this level of sonic energy on the large volumes associated with industrial waste.

3.2 Temperature effects

Calorimetric methods have long been used to determine energy produced during reactions. Application of this old technique to the field of sonochemistry allowed scientists to calculate the efficiency at which reactions take place. Using methacrylate (MME) Kuijpers *et al.* studied how temperature influences energy transfer and free radical production [7]. They showed no effect by temperature on the efficiency of energy transfer. However, temperature did play a role in MME free radical formation. The free radical scavenger 1,1-diphenyl-2-picrylhydrazyl releases heat as it reacts. This allows free radical release by MME to be equated with increases in temperature that is easily measured during calorimeter experiments. Measuring how solute temperature affects cavitation, and hence free radical production is simple. The reaction vessel, called a bomb, is equilibrated to the temperature in question prior to ultrasound treatment. Afterward the increase in temperature of the system is measured. The quantity of free radicals produced is then calculated using thermodynamic equations. Amplitude, or the displacement generated by a sound wave, is a physical property of the sonic burst that can have profound effects on the chemistry occurring in a solution. Higher amplitudes cause a greater fluctuation in cavity volume with each absorbed wave. This increases the energy delivered to a cavity, pushing them from a stable cavity to a transient one where free radicals can be produced [7]. **Figure 3.2** demonstrates the effect temperature on free radical formation at different amplitudes of sonic treatment. Higher free radicals production at lower temperatures is not surprising [7]. This is probably attributed to the solvent having less internal energy, which promotes the production of more high energy cavities that could generate increased free radical chemistry when they collapse.

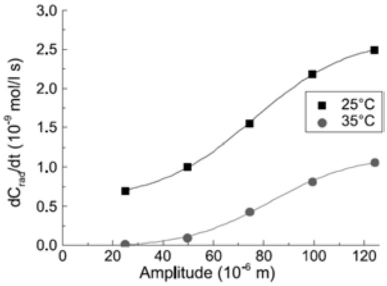

Figure 3.2: Radical formation rate as a function of the amplitude at two different temperatures in MMA [7].

3.3 Solutes and free radical generation effects:

Gases have an internal property known as thermal conductivity which can greatly affect cavity dynamics and free radical formation [9]. Kondo *et al.* studied how this property can influence hydroxyl radical formation by saturating water with monatomic gases: helium neon, argon, krypton and xenon (shown in order of decreasing thermal conductivity). Measurement of hydroxyl radical by ESR demonstrated that as thermal conductivity of a dissolved gas decreases, hydroxyl radical formation increases [9]. Conversely other studies have shown that dissolved gases can counter act the formation of free radicals. When Feril and colleagues dissolved carbon dioxide (CO_2) in a suspension of cells prior to ultrasound treatment they were able to inhibit cell death [3]. Measurement of free radicals by ESR showed that dissolved CO_2 blocked their formation and cell killing. Chemical reactions have even been observed on a single bubble to measure the generation of free radicals during sonochemical events. This was done by adding a new twist to a simple child's experiment. When elemental iodine (I_2) is added to a starch solution it turns blue, the result of a chemical reaction between starch and iodine. However, in a solution of starch and potassium iodine no color appears, because the iodine must first be converted from an ion to its elemental state, I_2. Carbon tetrachloride a compound that is insoluble in water, and readily forms radicals when subjected to acoustic cavitation which can facilitate the formation of I_2, as described in **Figure 3.3** [10]. Because of its insolubility in water, carbon tetrachloride coats the outside of any cavity that forms after high frequency acoustic energy is applied. This generates a "triple phase" system with carbon tetrachloride sequestered between the starch solution and the cavity. Therefore as radicals form they can generate I_2 locally, which quickly reacts with the starch in solution to form a blue filament that is observable on the bubble's surface [8].

$$2CCl_4 \xrightarrow{)))} C_2Cl_6 + 2Cl(\cdot)$$

$$Cl(\cdot) + I^- \rightarrow Cl^- + \tfrac{1}{2}I_2$$

Figure 3.3: Chemical reactions between carbon tetrachloride and Iodine ion where))) denotes a reaction activated by acoustic cavitation [8].

4. The biochemical effects of sonochemistry

Ultrasonic energy can also have dramatic effects on living organisms. Damage is initiated by both the formation of free radicals, and mechanical force [14]. This damage can serve both as friend, or foe. Sonochemistry induced oxidation has been applied to the problem of waste water management. Researches have used sonic energy in conjunction with photochemistry to effectively decontaminate water [11]. This process is carried is called the 'sonuv' reaction, where UV light produces compounds that sonochemistry can convert into hydroxyl radicals. In organisms, DNA is the biomolecule most sensitive to sonochemical treatment because damage can generate mutations that are passed on to the next generation or result in cell death. Base damage is the result of peroxide attack, and can yield many different products to induce mutations [12]. Most notable among these is 8-oxoguanine and 5,6 dihydroxydihydrothymine [12, 13]. Increased mutation rates by sonochemical events have their benefit, and have been recognized to have potential utility as a treatment for cancer. Mouse sarcomas cells treated with a range of ultrasound energy showed an increase in the amount of Thymine base damage (TBD). The addition of free radical scavengers blocked the formation of TBD, but did not increase cell survival [13]. This means that the prevalent mechanism for cell killing by high levels of ultrasonic energy is DNA sheering.

5. Summary

Sonochemistry is the study of chemical reactions that are initiated by treating a solution with high frequency ultrasound. Reactions are driven by thermal energy produced by the collapse of cavities in treated solutions [1]. Most of the chemistry produced is the result of free radical production which is initiated by intense thermal energy causing thermolysis of molecules in solution. As we look to the future the possibilities for sonochemistry seem endless, with applications in industry, environmental research, and medical treatments [4]. However, what makes this topic most exciting it the thought that bursting bubbles, a common playtime activity for children, can produce such large amounts of thermal energy.

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