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Review Article

Sonochemistry: Non-Classical Way of Synthesis

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ABSTRACT

This review presents the detailed picture of current knowledge on ultrasound assisted chemical reactions and its green approach in chemical synthesis. This article illustrates the theoretical background and details about ultrasound, its mechanism (cavitation, the driving force) in chemical synthesis, types of reactions with different systems and its utility. All the reported applications have shown that Sonochemistry, ultrasound assisted chemical reaction is a green and economical viable approach for drug, impurity or chemical intermediate synthesis.

Keywords: Cavitation, Sonocatalysis, Sonochemistry Ultrasound

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INTRODUCTION

In chemistry, the study of sonochemistry is related with understanding the effect of sonic waves and wave properties on chemical reactions. Ultrasound has proven to be a very useful tool in enhancing the reaction rates in a variety of reacting systems. It has successfully raised the conversion, improved the yield, changed the reaction pathway, and/or started the reaction in chemical, electrochemical and biological systems. This non classical method of rate enhancement, a field termed *sonochemistry*, is becoming a widely used laboratory technique. The term sonochemistry is used to describe a subject which uses sound energy to affect chemical processes. Thus sonochemistry is the application of ultrasound to chemical reaction and processes to enhance the reaction rate and to increase yield. The utilization of ultrasound may implement operation at mild operating situations (e.g., lower temperatures and

pressures), eliminate the need for extra costly solvents, reduces the number of synthesis steps while simultaneously increasing end yields, permit the use of lower purity reagents and solvents, and/or increase the activity of existing catalysts. For these reasons, use of ultrasound appears to be a promising alternative for high-value chemicals and pharmaceuticals.¹

RANGE OF ULTRASOUND

Ultrasound frequencies from about 20 kHz to 10 MHz which is the part of the sonic spectrum and can be approximately subgrouped in three main regions: high frequency, low power ultrasound (1 MHz to 10 MHz), high frequency, medium power ultrasound (100 kHz to 1 MHz) and low frequency, high power ultrasound (20 kHz to 100 kHz). The frequencies far more than 1 MHz are utilized as medical and diagnostic ultrasound and frequencies from 20 kHz to around 1 MHz is utilized in sonochemistry.¹

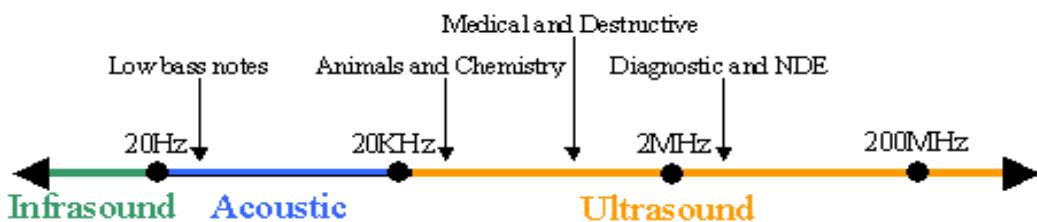


Figure 1: Range of Ultrasound waves.

• Cavitation: The Driving Force

One of the most basic concepts of sonochemistry is that free radicals are formed as a result of the cavitation of microbubbles which are created during the rarefaction (or negative pressure) period of sound waves. The whole body of knowledge of sonochemistry and all its applications is based on a single process cavitation. The mechanical and chemical actions of ultrasound are created by cavitation bubbles.

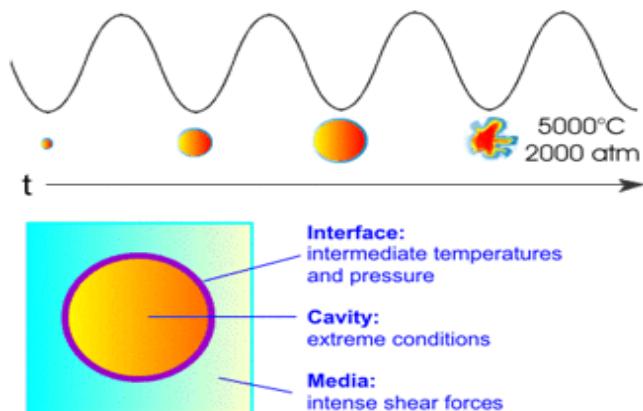


Figure 2: Cavitation

About irradiation with high strength ultrasound or sound, acoustic cavitation usually takes place. Cavitation – the generation, growth and implode collapse of bubbles irradiated with sound - is the impulsion for sonoluminescence (homogeneous sonochemistry of liquids) and sonochemistry. Bubble collapse in liquids makes vast amounts of energy from the conversion of kinetic energy of the liquid movement into warming the amounts of the bubble. The compression of the bubbles during cavitation is faster than thermal shift, which produces a short-lived localized hot-spot. Experimental data have shown that these bubbles have temperatures about 4726.85 °C, pressures of around 1000 atmosphere, and heating and cooling rates above 736.85 °C/s. These cavitations can generate extreme chemical and physical situations in otherwise cold liquids.

With liquids having solids, alike phenomena may produce with exposure to ultrasound. Once cavitation produces near an enlarged solid surface, cavity collapse is non-spherical and drives elevated-speed jets of liquid to the surface. These jets and related shock waves can damage highly warmed surface. Liquid-powder suspensions occur high intensity interparticle collisions. These collisions can vary the surface composition, morphology and reactivity.²

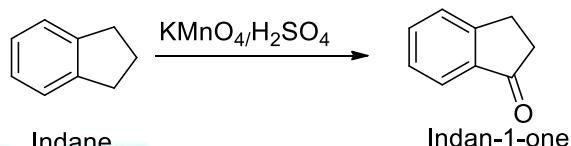
TYPES OF SONOCHEMICAL REACTIONS IN SYNTHESIS

Basically, there are 3 kinds of sonochemical process: homogenous sonoluminescence, heterogeneous sonochemistry (solid-liquid or liquid-liquid systems) and some kind that represents a combine of both homogeneous and heterogeneous sonochemistry (sonocatalysis).⁴

[A] Homogenous Reactions:

The use of ultrasound in aqueous solutions leads to the sonolysis of the components of the solution, such as $\text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}^+$.^[13] The enhancing effects of ultrasound in organic systems are not directly related to thermal effects but are instead a result of acceleration of the single-electron transfer (SET) process. The SET step is required as an initial step in several reactions, such as cycloadditions involving carbodienes and heterodienes.

Oxidation of indane to indan-1-one. By conventional method the yield of product is ≤ 27 % while in ultrasonic condition the yield is increased to 73 %.⁵



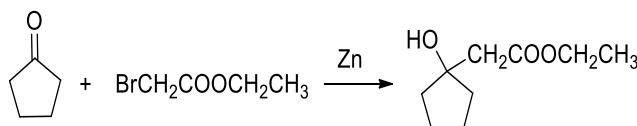
[B] Heterogeneous Systems:

(I) Liquid-Liquid Systems: Ultrasound forms very fine emulsions in systems with two immiscible liquids, which is very beneficial when working with phase-transfer-catalyzed or biphasic systems. When very fine emulsions are formed, the surface area available for reaction between the two phases is significantly increased, thus increasing the rate of the reaction. This aspect of ultrasound has also been used for coal, oil, and water mixtures to increase the efficiency of combustion, as well as decrease the amount of pollutants produced during the combustion process.

(II) Liquid-Solid Systems: The most pertinent effects of ultrasound on liquid-solid systems are mechanical and are attributed to symmetric and asymmetric cavitation. When a bubble is able to collapse symmetrically, localized areas of high temperatures and pressures are generated in the fluid. In addition, shock waves are produced which have the potential of creating microscopic turbulence within interfacial films surrounding nearby solid particles, also referred to as microstreaming. This phenomenon increases the transfer of mass across the film, thus increasing the intrinsic mass-transfer coefficient, as well as possibly thinning the film. When the solid is inorganic, the particles are fractured upon collision, leading to an overall decrease in the average particle size.

For example, the particle size of inorganic solid KOH was reduced from its initial size of 240 μm to 15-20 μm within 5 min of sonication.

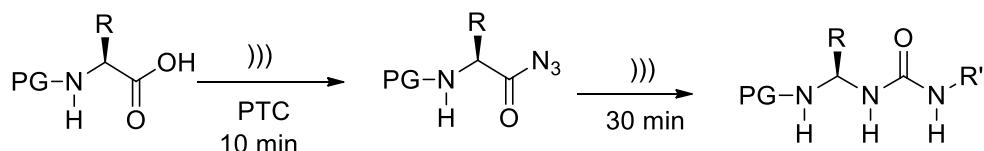
Reformatsky reaction In conventional method the reaction time is 12 hrs and the yield is only 58% while in ultrasound condition the time required is only 30 min with yield of 98%.⁶



Sonocatalysis: When the solid present in the medium acts as a catalyst, ultrasound can significantly influence the chemistry occurring within the system. The intensity of ultrasound can alter the stereoselectivity of a particular reaction, as observed in the case of the cyclization of the tetracyclic 19-iodotabersonine to the vindolinine epimers.

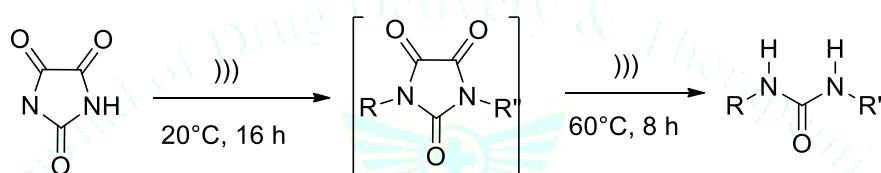
SONOCHEMISTRY IN LITERATURE

A facile one-pot synthesis of urea-linked peptidomimetics and neoglycopeptides carried out under Curtius rearrangement conditions employing Deoxo-Fluor and TMSN₃ under sonication is efficient and circumvents the isolation of acyl azide and isocyanate intermediates.⁷



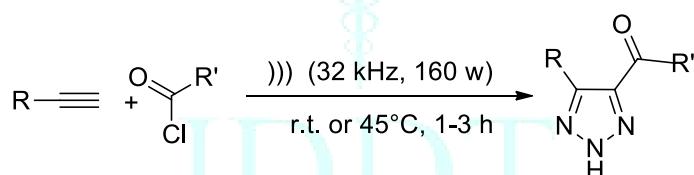
Synthesis of structurally and functionally diverse N-carbamoylamino acids through the alkylation of monosubstituted parabanic acids followed by hydrolysis of

the intermediate products using ultrasound gives very good yields and excellent purity.⁸



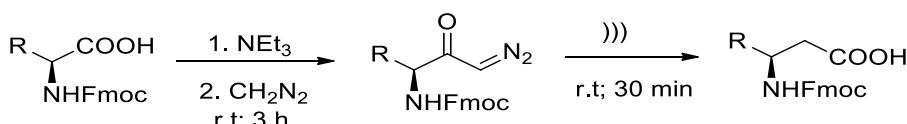
4,5-Disubstituted-1,2,3-(NH)-triazoles was synthesized in excellent yields by a palladium-catalyzed and ultrasonic promoted Sonogashira coupling/1,3-dipolar cycloaddition of

acid chlorides, terminal acetylenes, and sodium azide in one pot.⁹



Sonication of diazo ketones obtained from fmoc-protected amino acids in dioxane in the presence of water and silver benzoate results in clean production of the corresponding β -

amino acid derivatives. No substantial epimerization produced except for phenylglycine.¹⁰



APPLICATION OF SONOCHEMISTRY^{9,10}

Ultrasound in Life Sciences and Medicine:

- Ultrasound in Life Sciences and Medicine Sonophoresis
- Ultrasonic imaging.
- Ultrasound NMR. Diagnostic Ultrasound.
- Dental Scaling and Ultrasonic Nebulizers in medical therapy.
- Enzyme activation.

Application in Polymer Science and Technology:

- Power ultrasound in polymer technology
- Treatment of polymers,
- Treatment of plastics,
- Molecular weight reduction,
- Welding Enhanced radical polymerization,
- Reduction in Viscosity in Molding,
- Copolymerisation, Mixing of additives,
- Encapsulation Surface treatment.

Applications in Materials Science:

- (a) Applications in Materials Science Generation of activated metals by sonication. Sonolysis of organic pollutants in water.
- (b) Ultrasonic plastic and metal welding,
- (c) Machining,
- (d) Ultrasonic soldering.
- (e) Sonocleaning.

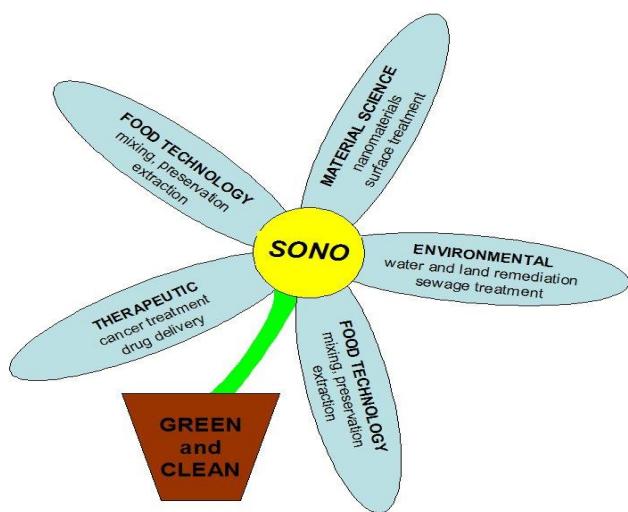


Figure: 3 Application of Sonochemistry

CONCLUSION

Sonochemistry is gaining significance based on laboratory results and the availability of scale-up systems. Sonochemical applications can be envisaged in all types of systems, including homogenous reactions. Wide acceptance has been gained at a practical/empirical level, however, the theoretical understanding still lags significantly behind. The

usefulness of sonochemistry continues to expand into the arena of electrochemistry, photochemistry and biotechnology.

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