Ultrasound: A Boon in the Synthesis of Organic Compounds

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The use of ultrasound for promoting chemical reactions is described.

Ultrasound is the name given to sound waves having frequencies higher than those to which human ears can respond, i.e. greater than 16kHz and with wavelength between 7.0 and 0.015 cm. It is transmitted through any substance – solid, liquid or gas, which possesses elastic properties. The first commercial application of ultrasonics appeared in 1917 with Langevin's echo-sound technique for the estimation of depths of water resulting in the system known as SONAR (sound navigation and ranging). Some of the broader applications of ultrasound in various fields are for homogenisation and cell disruption in *biology and biochemistry*; to assist in drilling, grinding, cutting, welding of hard materials and testing of materials in *engineering*; for cleaning and drilling teeth in *dentistry;* for dispersal of pigments and solids in paints, inks, resins; for acoustic filtration and ultrasound drying in *industry*; for ultrasound imaging in obstetrics and treatment of muscle strains in *medicine* (frequency range 1 – 10 MHz); for welding of thermoplastics, polymer degradation, curing of resins and initiation of polymerisation in *plastics and polymers* ; for breakdown of aromatic pollutants and cell disruption of bacteria in *waste treatment,* to name a few.

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Ultrasound has also been employed for specific chemical applications. The chemical effects of ultrasound were first reported by A L Loomis in 1927. The hydrolysis of dimethyl sulphate and the iodine clock reaction were found to be accelerated by ultrasound. Initially, the use of ultrasound was restricted. However, it has increased manifold in a variety of chemical reactions, resulting in a sub-discipline called 'Sonochemistry'.

In this article, the chemical consequences of ultrasound are described. We begin with a process known as cavitation which is responsbile for the chemical effects. Later, applications of sonochemistry are presented with a few representative examples.

Cavitation

As stated earlier, ultrasound waves can be transmitted through any material possessing elastic character. The movement of the sound source is transmitted to the particles of the medium, which oscillate in the direction of the wave and produce longitudinal waves as well as transverse waves as shown in *Figure 1.*

As the molecules of the medium vibrate, the average distance between the molecules decreases in the compression cycle and increases during rarefaction. When the average distance between the molecules exceeds the critical molecular distance necessary to hold the liquid intact, the liquid breaks down; cavities (cavitation) and bubbles are formed. This process, known as cavitation, refers to the formation and the subsequent dynamic life of bubbles in liquids. These bubbles can be filled with gas or vapour and occur in water, organic solvents, biological fluids, liquid helium, molten metals or other fluids. Bubble collapse results in high temperature (as much as 4700°C) and pressure changes (10Pa). The solvent/reagent vapour suffers fragmen-

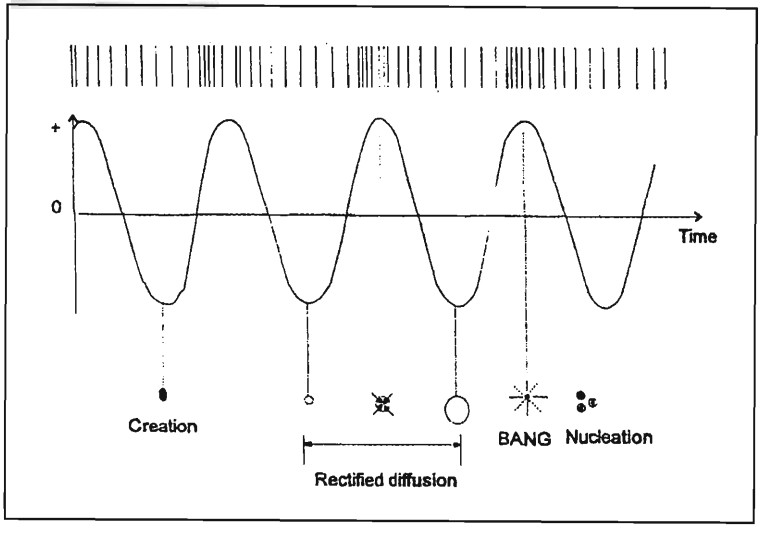


Figure 1. Lifetime of an 'Acoustic Transient Cavitation' Bubble.

A number of common reactions used in synthetic organic chemistry can be carried out more efficiently using ultrasound.

tation to generate reactive species, such as free radicals or carbenes. These high-energy species are concentrated at the interface and lead to intermolecular reactions. However, if there are involatile solutes, they would also collect at the interface and react with the high energy species. Besides this, the shock wave produced by a bubble collapse can influence the reactivity by altering the solvation of the reactive species.

Ultrasound Sources

A variety of devices have been used for ultrasonic irradiation of solutions. For common laboratory use, there are three main designs (a) ultrasonic cleaning bath (b) cup horn sonicator, and (c) direct immersion ultrasonic horn. The source of the ultrasound is a piezoelectric material (lead-zirconate-titanate ceramic (PZT) or quartz) which is subjected to high voltage alternating current with an ultrasonic frequency (15 kHz – 10MHz). The piezoelectric material expands and contracts in this electric field and is attached to the walls of the cleaning bath (or amplifying horn) and converts electrical energy into sound energy. In most applications the sonicators operate at a fixed frequency in the range of 20 – 35 kHz. In cleaning baths the acoustic field is continuous whereas it is in the pulsed form in probes.

In the ultrasonic cleaning bath (*Figure 2*) a liquid (H_2O) is present for transferring the ultrasound from the generators to the reaction vessel. The reaction vessel (conical or R B flask) is submerged in the water at a level where the liquid in the flask is just above the surface of the water. After sonication is started, the flask is adjusted to the point where cavitation (bubbles) is maximum. The temperature of the water is kept constant by cooling. Results obtained by using a cleaning bath are not always reproducible and therefore at times the use of sonic probes (*Figure 3*) is preferred.

Reactions Accelerated by Ultrasound

A number of common reactions used in synthetic organic chemistry can be carried out more efficiently using ultrasound.

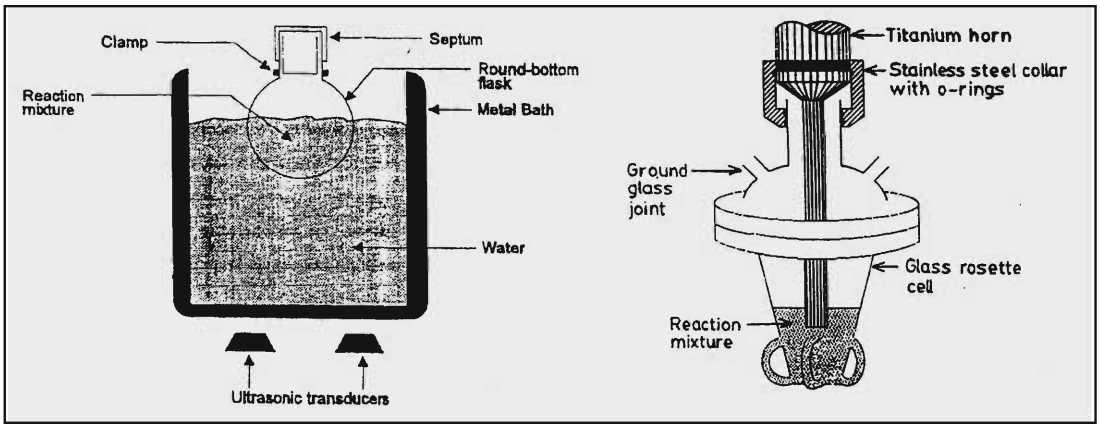


Figure 2(left). Apparatus for carrying out a reaction in an ultrasonic cleaning bath.

Figure 3 (right). Suslick cell apparatus attached to a sonic probe for use in small-scale reactions in an inert atmosphere.

There are several advantages. Generally, the yield increases and the percentage of by-products decreases. Reactions occur faster, so that lower temperatures can be used. Ultrasound provides alternative pathways for reactions, due to the formation of high energy intermediates. Sonochemistry also enables reactions involving organometallic reagents to be carried out safely. In the following text several specific applications are provided.

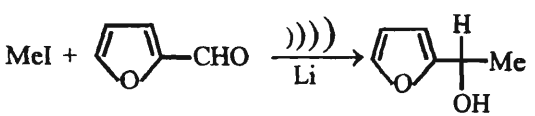
The reaction of magnesium with ethyl, butyl and phenyl bromides in aqueous diethyl ether or in *n*-dibutyl ether containing 50% benzene or light petroleum is accelerated by utilising ultrasound.

$$R{-}X + Mg \xrightarrow{))))} R{-}Mg{-}X$$

$R = C_2H_5, n\text{-}C_4H_9, C_6H_5$

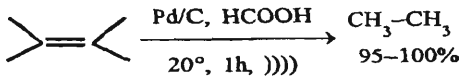
$X = Cl, Br$

In late 1980, Luche published a communication describing the beneficial effects of ultrasonic waves on the lithium modified Barbier reaction giving excellent yields.



10 min, 100%

Formic acid and palladium on carbon are an effective couple for the hydrogenation of a wide range of alkenes at room temperature in the presence of low intensity ultrasonic fields (cleaning bath, 50kHz).



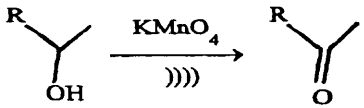
Suggested Reading

[1] T J Mason and J P Lorimer. *Sonochemistry: Theory, Applications and Uses of Ultrasound in Chemistry.* Ellis Horwood Ltd., 1988.

[2] K S Suslick. *Ultrasound, its Chemical, Physical and Biological Effects.* VCH Publishers, Inc., 1988.

[3] M A Margulis. *Advances in Sonochemistry.* T J Mason ed., 1,49, London and Greenwich, Connecticut, JA 1, 1990.

The oxidation of alcohols by solid potassium permanganate in hexane and benzene is significantly enhanced by sonication in an ultrasonic bath.



The Reformatsky reaction can be carried out in high yield (98%) in just 30 minutes at 25–30° C as compared to conventional method, which gives only 50% yield after 12 hours at 80°C.

$$C_4H_8C{=}O + BrCH_2COOEt + Zn \xrightarrow{NaX} C_4H_8C(OH)CH_2COOEt$$

Similarly, in the breakdown of polymeric organotin fluoxides, there is 900 fold increase in rate as compared to conventional reflux.

$$[R_3SnF]_n \longrightarrow nR_3SnX$$

R=Me, n–Bu or Ph

X=Cl, Br, NCO

Sonochemical Boon

In addition to the types of reactions mentioned above, ultrasound has also been used in the case of enzyme catalysed reactions. There are a large number of other such reactions in non-aqueous solvents where ultrasound has been used over the last few years. For example conjugate addition of alkyl groups to α, β-unsaturated compounds is under extensive study.

Application of sonochemical principles in polymer chemistry and coal liquification has been reported. Extension of combination of sonochemistry with other specific methods, such as photochemistry and electrochemistry appears to be promising.

Since it is an upcoming and a recent field of interest, there is a great deal more to explore in ultrasonics as an important tool in order to tap its full potential for the discovery of new reactions utilising highly energetic sound waves. The sonochemical boom is turning out to be a real boon for synthetic chemistry.

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