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Sonochemistry: The effect of sonic waves on chemical systems

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Abstract

Sonochemistry is the application of ultrasound to chemical reactions and processes. The mechanism causing sonochemical effects in liquids is the phenomenon of acoustic cavitation. The chemical effects of ultrasound do not come from a direct interaction with molecular species. Studies have shown that no direct coupling of the acoustic field with chemical species on a molecular level can account for sonochemistry or sonoluminescence. Cavitation the formation, growth, and implosive collapse of bubbles irradiated with sound is the impetus for sonochemistry and sonoluminescence. Sonochemistry can be performed by using a bath (usually used for ultrasonic cleaning) or with a high power probe.

1. Sonochemistry

1.1 Introduction

In chemistry, the study of sonochemistry is concerned with understanding the effect of sonic waves and wave properties on chemical systems. The chemical effects of ultrasound do not come from a direct interaction with molecular species. Studies have shown that no direct coupling of the acoustic field with chemical species on a molecular level can account for sonochemistry or sonoluminescence[1,2]. Instead, sonochemistry arises from acoustic cavitation: the formation, growth, and implosive collapse of bubbles in a liquid.

This is demonstrated in phenomena such as ultrasound, sonication, sonoluminescence, and sonic cavitation. Sonochemistry is that branch of one, which deals with the study of sonic waves and their properties on chemical systems.

The influence of sonic waves traveling through liquids was first reported by Robert Williams Wood (1868-1955) and Alfred Lee Loomis (1887-1975) in 1927, but the article was left mostly unnoticed[3]. Sonochemistry experienced a renaissance in the 1980s with the advent of inexpensive and reliable generators of high-intensity ultrasound.

Upon irradiation with high intensity sound or ultrasound, acoustic cavitation usually occurs. Cavitation: the formation, growth, and implosive collapse of bubbles irradiated with sound is the impetus for sonochemistry and sonoluminescence[4]. Bubble collapse in liquids produces enormous amounts of energy from the conversion of kinetic energy of the liquid motion into heating the contents of the bubble. The compression of the bubbles during cavitation is more rapid than thermal transport, which generates a short-lived localized hot-spot. Experimental results have shown that these bubbles have temperatures around 5000 K, pressures of roughly 1000 atm, and heating and cooling rates above 10^{10} K/s[5]. These cavitations can create extreme physical and chemical conditions in otherwise cold liquids. With liquids containing solids, similar phenomena may occur with exposure to ultrasound. Once cavitation occurs near an extended solid surface, cavity collapse is nonspherical and drives high-speed jets of liquid to the surface[6]. These jets and associated shock waves can damage the now highly heated surface. Liquid-powder suspensions produce high velocity interparticle collisions. These collisions can change the surface morphology, composition, and reactivity[7].

Three classes of sonochemical reactions exist: homogeneous sonochemistry of liquids, heterogeneous sonochemistry of liquid-liquid or solid-liquid systems, and, overlapping with the aforementioned, sonocatalysis[8,9]. Sonoluminescence is typically regarded as a special case of homogeneous sonochemistry[10]. The chemical enhancement of reactions by ultrasound has been explored and has beneficial applications in mixed phase synthesis, materials chemistry, and biomedical uses. Because cavitation can only occur in liquids, chemical reactions are not seen in the ultrasonic irradiation of solids or solid-gas systems.

For example, in chemical kinetics, it has been observed that ultrasound can greatly enhance chemical reactivity in a number of systems by as much as a million-fold; effectively acting as a catalyst by exciting the atomic and molecular modes of the system (such as the vibrational, rotational, and translational modes)[11]. In addition, in reactions that use solids, ultrasound breaks up the solid pieces from the energy released from the bubbles created by cavitation collapsing through them. This gives the solid reactant a larger surface area for the reaction to proceed over, increasing the observed rate of reaction. Sonochemistry can be performed by using a bath (usually used for ultrasonic cleaning) or with a high power probe.

The use of ultrasound in chemical reactions in solution provides specific activation based on a physical phenomenon: acoustic cavitation. Cavitation is a process in which mechanical activation destroys the attractive forces of molecules in the liquid phase. Applying ultrasound, compression of the liquid is followed by rarefaction (expansion), in which a sudden pressure drop forms small, oscillating bubbles of gaseous substances. These bubbles expand with each cycle of the applied ultrasonic energy until they reach an unstable size; they can then collide and/or violently collapse.

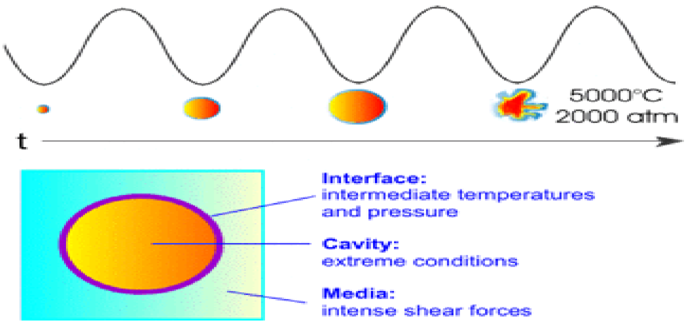


Figure-1

For example, sonolysis of $Fe(CO)_5$ in decane under argon produces amorphous iron upon decarbonylation instead of crystalline iron, which shows that both very high temperatures and also rapid cooling rates (~ 10^6 K s^{-1}) are involved, the more volatile pentane yields $Fe_3(CO)_{12}$, indicating a somewhat slower collapse. It has been estimated and calculated that the pressure within a bubble in water can rise to more than one thousand atmospheres, and the temperature can reach several thousand degrees during a collapse, as heat conduction cannot keep up with the resulting adiabatic heating. As these bubbles are small and rapidly collapse, they can be seen as microreactors that offer the opportunity of speeding up certain reactions and also allow mechanistically novel reactions to take place in an absolutely safe manner.

Many reactions can be conducted even in a simple ultrasonic cleaning bath, although the amount of energy that reaches the reaction is only between 1 and 5 W cm^{-2}, and temperature control is normally poor. Large-scale reactions can be better conducted using immersible ultrasonic probes that circumvent the transfer of the energy through water and the reaction vessel. The applied energies in this case can be several hundred times higher. Laboratory equipment uses frequencies between 20 kHz and 40 kHz, but cavitation can be generated well above these frequencies and recent research uses a much broader range.

1.2 Ultrasound in synthetic organic chemistry

There are two types of effects mediated by ultrasound: chemical and physical. When the quantity of bubbles is low - using standard laboratory equipment - it is mainly physical rate acceleration that plays a role. For example, a specific effect is the asymmetric collapse near a solid surface, which forms microjets. This effect is the reason why ultrasound is very effective in cleaning, and is also responsible for rate acceleration in multiphasic reactions, since surface cleaning and erosion lead to improved mass transport.

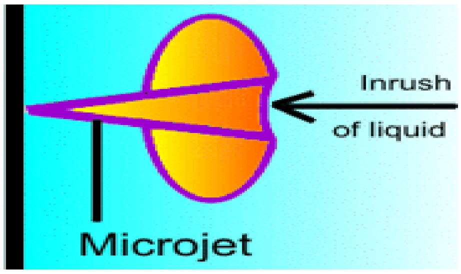
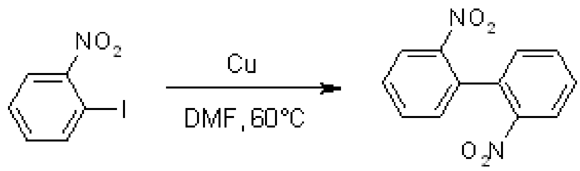


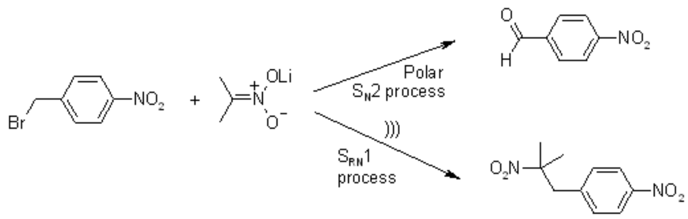
Figure-2

For example, when ultrasound is applied to an Ullmann reaction that normally requires a 10-fold excess of copper and 48 h of reaction time, this can be reduced to a 4-fold excess of copper and a reaction time of 10 h. The particle size of the copper shrinks from 87 to 25 µm, but the increase in the surface area cannot fully explain the increase in reactivity. It was suggested that sonication also assists in the breakdown of intermediates and desorption of the products from the surface.



Scheme-1

Typically, ionic reactions are accelerated by physical effects - better mass transport - which is also called "False Sonochemistry". If the extreme conditions within the bubble lead to totally new reaction pathways, for example via radicals generated in the vapor phase that would only have a transient existence in the bulk liquid, we speak about "sonochemical switching". Such a switch has been observed for example in the following Kornblum-Russel reaction where sonication favors an SET pathway:



Scheme-2

Applications for sonochemistry can be found in many areas, but sonochemical processes are most widely developed for heterogeneous reactions. Currently, sonochemistry is a multidisciplinary field in which chemists, physicists, chemical engineers and mathematicians must cooperate to develop a better understanding of the processes that take place within the collapsing bubbles to develop totally new applications. However, the potential for making improvements in many types of reaction suggests that every chemical laboratory should be equipped with at least one cleaning bath for simple trials[12].

2. Sonochemical Reaction and Synthesis

Sonochemistry is the application of ultrasound to chemical reactions and processes. The mechanism causing sonochemical effects in liquids is the phenomenon of acoustic cavitation. Hielscher ultrasonic laboratory and industrial devices are used in a wide range of sonochemical processes.

2.1 Sonochemical Reactions

The following sonochemical effects can be observed in chemical reactions and processes:

- increase in reaction speed
- increase in reaction output
- more efficient energy usage
- sonochemical methods for switching of reaction pathway
- performance improvement of phase transfer catalysts
- avoidance of phase transfer catalysts
- use of crude or technical reagents
- activation of metals and solids
- increase in the reactivity of reagents or catalysts
- improvement of particle synthesis
- coating of nanoparticles

2.2 Ultrasonic Cavitation in Liquids

Cavitation that is "the formation, growth, and implosive collapse of bubbles in a liquid. Cavitational collapse produces intense local heating (~5000 K), high pressures (~1000 atm), and enormous heating and cooling rates (>109 K/sec)" and liquid jet streams (~400 km/h). Cavitation bubbles are vacuum bubbles. The vacuum is created by a fast moving surface on one side and an inert liquid on the other. The resulting pressure differences serve to overcome the cohesion and adhesion forces within the liquid. Cavitation can be produced in different ways, such as Venturi nozzles, high pressure nozzles, high velocity rotation, or ultrasonic transducers. In all those systems the input energy is transformed into friction, turbulences, waves and cavitation. The fraction of the input energy that is transformed into cavitation depends on several factors describing the movement of the cavitation generating equipment in the liquid.

The intensity of acceleration is one of the most important factors influencing the efficient transformation of energy into cavitation. Higher acceleration creates higher pressure differences. This in turn increases the probability of the creation of vacuum bubbles instead of the creation of waves propagating through the liquid. Thus, the higher the acceleration the higher is the fraction of the energy that is transformed into cavitation. In case of an ultrasonic transducer, the intensity of acceleration is described by the amplitude of oscillation. Higher amplitudes result in a more effective creation of cavitation. The industrial devices of Hielscher Ultrasonics can create amplitudes of up to 115 µm. These high amplitudes allow for a high power transmission ratio what in turn allows to create high power densities of up to 100 W/cm^3. In addition to the intensity, the liquid should be accelerated in a way to create minimal losses in terms of turbulences, friction and wave generation. For this, the optimal way is a unilateral direction of movement.

Ultrasound is used because of its effects in processes, such as:
- preparation of activated metals by reduction of metal salts
- generation of activated metals by sonication
- sonochemical synthesis of particles by precipitation of metal (Fe, Cr, Mn, Co) oxides, e.g. for use as catalysts
- impregnation of metals or metal halides on supports
- preparation of activated metal solutions
- reactions involving metals via in situ generated organoelement species
- reactions involving non-metallic solids
- crystallization and precipitation of metals, alloys, zeolithes and other solids
- modification of surface morphology and particle size by high velocity interparticle collisions

o formation of amorphous nanostructured materials, including high surface area transition metals, alloys, carbides, oxides and colloids
o agglomeration of crystals
o smoothing and removal of passivating oxide coating
o micromanipulation (fractionation) of small particles
- dispersion of solids
- preparation of colloids (Ag, Au, Q-sized CdS)
- intercalation of guest molecules into host inorganic layered solids
- sonochemistry of polymers
o degradation and modification of polymers
o synthesis of polymers
- sonolysis of organic pollutants in water

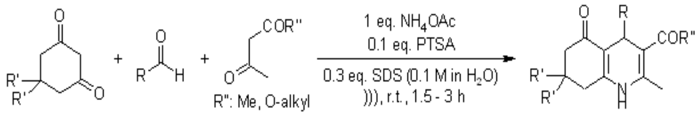
2.3 Sonochemical Equipment

Most of the mentioned sonochemical processes can be retrofitted to work inline. We will be glad to assist you in choosing the sonochemical equipment for your processing needs. For the research and for the testing of processes we recommend our laboratory devices or the UIP1000hd set. If required, FM and ATEX certified ultrasonic devices and reactors (e.g. UIP1000-Exd) are available for the sonication of flammable chemicals and product formulations in hazardous environments.

2.4 Ultrasonic Cavitation Changes Ring-Opening Reactions

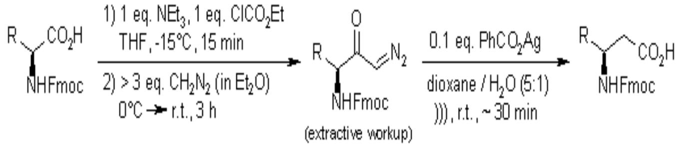
Ultrasonication is an alternative mechanism to heat, pressure, light or electricity to initiate chemical reactions. Jeffrey S. Moore, Charles R. Hickenboth, and their team at the Chemistry Faculty at University of Illinois at Urbana-Champaign used ultrasonic power to trigger and manipulate ring-opening reactions. Under sonication, the chemical reactions generated products different from the the ones predicted by orbital symmetry rules (Nature **2007**, 446, 423). The group linked mechanically sensitive 1,2-disubstituted benzocyclobutene isomers to two polyethylene glycol chains, applied ultrasonic energy, and analyzed the bulk solutions by using C^{13} nuclear magnetic resonance spectroscopy. The spectra showed that both the cis and trans isomers provide the same ring-opened product, the one expected from the trans isomer. While thermal energy causes random Brownian motion of the reactants, the mechanical energy of ultrasonication provides a direction to atomic motions. Therefore, cavitational effects efficiently direct the energy by straining the molecule, reshaping the potential energy surface [13].

3. Recent Literature



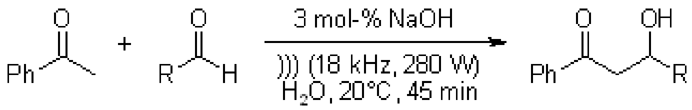
Scheme-3

Hantzsch 1,4-dihydropyridine and polyhydroquinoline derivatives were synthesized in excellent yields in aqueous micelles. The reaction is catalyzed by PTSA and strongly accelerated by ultrasonic irradiation[14].



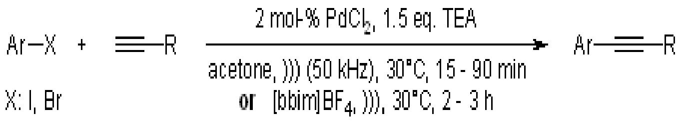
Scheme-4

Sonication of diazo ketones derived from Fmoc-protected amino acids in dioxane in the presence of silver benzoate and water results in clean formation of the corresponding β-amino acid derivatives. The degree of racemization was examined using capillary zone electrophoresis. No substantial epimerization occured except for phenylglycine[15].



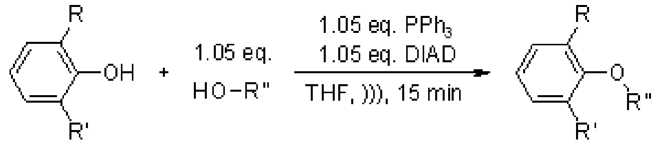
Scheme-5

High-intensity ultrasound was employed to reinvestigate the aldol reaction in water. A number of aldols that would eliminate or form side products under conventional conditions were isolated in good yields within minutes. The results are highly reproducible because the sonochemical parameters were rigorously controlled[16].



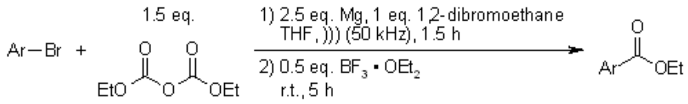
Scheme-6

The Sonogashira reaction proceeds efficiently at ambient temperature in acetone or 1,3-di-n-butylimidazolium tetrafluoroborate ([bbim]BF_4, a room-temperature ionic liquid) under ultrasound irradiation in the absence of a copper cocatalyst and a phosphine ligand[17].



Scheme-7

A vast rate increase has been achieved by the use of high concentration combined with sonication in the Mitsunobu reaction of phenols with alcohols where at least one substrate is sterically demanding[18].



Scheme-8

Sonication of a mixture of magnesium powder, 1,2-dibromoethane, aryl bromide and diethyl dicarbonate in THF followed by treatment with $BF_3 \cdot OEt_2$ at room temperature afforded aryl ester with reasonable yield. A series of aryl bromides were investigated and transformed to their corresponding aryl esters[19].

Conclusion

Sonochemistry is a multidisciplinary field in which chemists, physicists, chemical engineers and mathematicians must cooperate to develop a better understanding of the processes that take place within the collapsing bubbles to develop totally new applications. Thus, sonochemistry has been explored and has beneficial applications in mixed phase synthesis, materials chemistry, and biomedical uses.

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