Sonochemistry - Introduction

Fundamentals

What is Sonochemistry ?

Sonochemistry is the application of ultrasound to chemical reactions and processes. Ultrasound is the part of the sonic spectrum which ranges from about 20 kHz to 10 MHz and can be roughly subdivided in three main regions: low frequency, high power ultrasound (20-100 kHz), high frequency, medium power ultrasound (100 kHz-1 MHz), and high frequency, low power ultrasound (1-10 MHz). The range from 20 kHz to around 1 MHz is used in sonochemistry wheras frequencies far above 1 MHz are used as medical and diagnostic ultrasound.
Acoustic Cavitation

The origin of sonochemical effects in liquids is the phenomenon of acoustic cavitation. The term cavitation comes from the latin word cavus = cavity. Acoustical energy is mechanical energy i.e. it is not absorbed by molecules. Ultrasound is transmitted through a medium via pressure waves by inducing vibrational motion of the molecules which alternately compress and stretch the molecular structure of the medium due to a time-varying pressure. Therefore, the distance among the molecules vary as the molecules oscillate around their mean position. If the intensity of ultrasound in a liquid is increased, a point is reached at which the intramolecular forces are not able to hold the molecular structure intact. Consequently, it breaks down and a cavity is formed. This cavity is called cavitation bubble as this process is called cavitation and the point where it starts cavitation threshold. A bubble responds to the sound field in the liquid by expanding and contracting, i.e. it is excited by a time-varying pressure.Two forms of cavitation are known: stable and transient. Stable cavitation means that the bubbles oscillate around their equilibrium position over several refraction/compression cycles. While transient cavitation, the bubbles grow over one (sometimes two or three) acoustic cycles to double their initial size and finally collapse violently.

The size, life time and fate of a cavitation bubble depend on the following parameters: frequency, intensity (acoustic pressure), solvent, bubbled gas, external parameter (temperature, pressure). However, it should be noted that there is often no simple relationship.

For some images on the cavitational collapse see the special page on images of sonochemistry and sonoluminescence.

Physical Effects

There are three different theories about cavitation - the hot-spot, the electrical and the plasma theory. The most popular one is the hot spot theory. Thus, it has been experimentally shown that the cavitational collapse creates drastic conditions inside the medium for an extremely short time: temperatures of 2000-5000 K and pressures up to 1800 atm inside the collapsing cavity. A remarkable event during the cavitation collapse is the emission light under certain conditions (sonoluminescence). Furthermore, the collapse causes a couple of strong physical effects outside the bubble: shear forces, jets and shock waves. Thus, there are basically two groups of effects: radical and mechanical effects. These cavitation-induced effects can cause physical, chemical, and biological effects. Thus, ultrasound has been found applications in chemistry, materials and life sciences as well as medicine.

Chemical Effects

There is no doubt that the origin of sonochemical effects is cavitation. There a three possible reaction sides of a collapsing bubble: the cavity interior, the bubble vicinity and the bulk solution. Due to the extreme conditions inside the medium and other cavitation effects the following effects depending on the sonication conditions have been found :

i. radical effects

ligand-metal bond cleavage in transition metal complexes to give coordinatively unsaturated species or modified complexes as well as complete strip off of ligands to produce amorphous metals
disrupture of the solvent structure altering the solvation of reactants
sonolysis of molecules (homolytic fragmentation to radicals, rupture of polymers, generation of excited states, cell disrupture);

ii. mechanical effects

mechanical effects by cavity collapse onto metals and solids (shear forces, jets and shock waves resulting in rapid mass transfer, surface cleaning, particle size reduction and metal activation), modification of the properties of solid particles;

iii. influence on electrochemical processes

effects in liquid-liquid systems (improved mass transfer, emulsification, increase of the effect of phase transfer catalysts or even their replacement
effects in gas-liquid systems (degassing of liquids or melts, atomisation of liquids in air, thin film preparation)
single electron transfer (SET) steps in chemical reactions may be accelerated and if an ionic and an electron transfer pathway are possible the latter seems to be preferred ("sonochemical switching").

Ultrasound in Chemistry, Materials and Life Sciences

There are a wide range of applications of ultrasound in these fields. Therefore, only a selection of important and interesting examples and effects are given in the following to show the far range of possible applications and just to give an impression what ultrasound/sonochemistry means.

Applications in Chemistry

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

decrease of reaction time and/or increase of yield
use of less forcing conditions e.g. lower reaction temperature
possible switching of reaction pathway
use of less or avoidance of phase transfer catalysts
degassing forces reactions with gaseous products
use of crude or technical reagents
activation of metals and solids
reduction of any induction period
enhancement of the reactivity of reagents or catalysts
generation of useful reactive species

Applications in Materials Science

There are some obstacles if a reaction should proceed between a solid and a liquid (or in a liquid dissolved) reactant in a heterogeneous system: the small surface area of a bulk solid, the solid surface may be coated by oxide layers or impurities, species have to diffuse to and away from the solid surface, deposition of products may inhibit further reactions. Applications of ultrasound to such systems are:

preparation of activated metals by reduction of metal salts (e.g. reduction with Li in THF to RIEKE-type powders or with formaldehyde to Pd or Pt), generation of activated metals by sonication, precipitation of metal (Cr, Mn, Co) oxide catalysts, impregnation of metals or metal halides on supports
preparation of activated metal solutions (e.g. colloidal alkali metal solutions, suspension of Mg or Hg), preparation of organometallic compounds from main group or transition metals, sonochemical reactions involving metals via in situ generated organoelement species, reactions involving non-metallic solids
crystallisation and precipitation of metals, alloys, zeolithes and other solids, agglomeration of crystals, degassing of melts, spray pyrolysis to form thin films or fine particles, treatment of solid surfaces, dispersion of solids, preparation of colloids (Ag, Au, Q-sized CdS)
ultrasonic sieving, filtration and micromanipulation (transportation, concentration, fractionation) of small particles, intercalation of guest molecules into host inorganic layered solids, ultrasonic-aided development in advanced lithography, electroless plating, wetting and impregnation

sonochemistry of polymers consisting of three main fields: the degradation and modification of polymers, the ultrasonically assisted synthesis of polymers and the determination of the polymer structure
sonolysis of organic pollutants in water has become a developing field of research in environmental technology
ultrasonic plastic and metal welding, machining, ultrasonic soldering
sonocleaning
spraying, metal welding, machining and surface hardening

ultrasound food technology (fields of interest: mixing, blending, extraction, crystallisation, foam destruction, particle/aerosol precipitation, oxidation)

Ultrasound in Life Sciences and Medicine

Firstly, applications without any destruction or damage on living tissues :
disturbing of dermal cell membranes used for drug delivery (sonophoresis)
ultrasonic imaging
ultrasound nmr
diagnostic ultrasound
dental scaling and ultrasonic nebulizers in medical therapy
enzyme activation
Secondly, ultrasound caused damage on living tissues :
cell disrupture (extraction of plant substances, disinfecting, enzyme deactivation)
therapeutic ultrasound, i.e. induction of thermolysis in tissues (cancer treatment)
Thirdly, sonochemical preparation of biomaterials
air-filled protein microbubbles
nonaqueous liquid-filled protein microcapsules

Sonoluminescence

There are two forms of sonoluminescence: single-bubble SL and multi-bubble SL. Sonoluminescence was first discovered in 1930s. But, only in the late 1980's an intensive research started. The first researchers saw multiple-bubble sonoluminescence (MBSL), i.e. the glow from many bubbles of air in water. Since the glow for these bubbles is so faint, it must be viewed in a darkened room. Single-bubble sonoluminescence (SBSL), however, can be seen in a lighted room. 1990, however, was the first year that SBSL was observed, discovered by Gaitan and Crum, who after extensive research, found just the right conditions for SBSL to occur. To create SBSL, a single bubble of gas must be placed in the liquid. This can be done by injecting a bubble of air with a syringe, but researchers today use more elaborate setups. After being injected into the center of a cylindrical flask, the bubble would normally rise, but it is held in place by the force of the sound waves bombarding it. Around 110 decibels are required for sonoluminescence, and while this volume might seem high enough to cause deafness, the frequency of the sound is also important for SL, and it lies just beyond the range of human hearing. Putterman and his group discovered that the light flashes have an upper bound of 50 picoseconds (ps), and these flashes come out with incredible regularity.

For a detailed introduction look on other SL-websites.

For some images on SL see the special page on images of sonochemistry and sonoluminescence.

Historical Milestones

1867 Early observations of cavitation (TOMLINSON, GERNEZ)
1880 Discovery of the piezoelectric effect
1883 Earliest ultrasonic transducer by GALTON
1894 Cavitation as phenomenon recognized and investigated on propeller blades of HMS Daring (THORNYCROFT and BARVABY, Minutes of Proceedings of the Institution of Civil Engineers 122 (1895) 51)
1915-17 Pioneering work on ultrasonic acoustics by LANGEVIN
1917 First mathematical model for cavitational collapse predicting enormous local temperatures and pressures (RAYLEIGH)
1927 First paper on chemical effects of ultrasound published (RICHARDS and LOOMIS, J. Am. Chem. Soc. 49 (1927) 3086)
1933-35 Observation of sonoluminescence effects
1933 Reports on the reduction in the viscosity of polymer solutions by ultrasound
1943 First Patent on cleaning by ultrasound (German Pat. 733.470)
1944 First patent on emulsification by ultrasound (Swiss Pat. 394.390)
1950s Intensification of cavitation and ultrasound research, increasing number of applications using ultrasound
1950 Effect of ultrasound on chemical reactions involving metals (RENAUD, Bull. Soc. Chim. Fr. (1950) 1044)
1950 Hot spot model (NOLTINGK and NEPPIRAS)
1953 First review on the effects of ultrasound (BARNARTT, Quart. Rev. 7 (1953) 84)
1963 Introduction of plastic ultrasonic welding
1964 First monograph on physical, chemical and biological effects of ultrasound (ELPINER)
1970s Renaissance of sonochemistry research
since 1980 Growing research on sonochemical effects
1986 First ever international meeting on sonochemistry
1990 Foundation of the European Society of Sonochemistry and ESS 1 Meeting