

Sonochemistry: Scope, Limitations... and Artifacts

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Abstract. Heterogeneous sonochemistry, generally described as the most useful aspect of sonochemistry, suffers from the difficulty of defining the experimental conditions for the reference (silent) reaction. Clearly the use of an efficient agitation system for the silent reaction strongly reduces the value of the so-called sonochemical effect, which becomes in some cases, less than 1 (anti-sonochemical effect!). The 'cleaning' effect of ultrasound is extremely efficient to expel micro-crystals from the surface of an electrode which is simultaneously an immersion ultrasonic horn. By sending out-of-phase electric pulses and acoustic pulses, new nano materials (metals, alloys, semiconductors, oxides) are easily prepared in high purity.

Keywords: COST · Sonochemistry

Sonochemistry is a sub-domain of liquid-phase chemistry which is mainly focused on the effects of sound or ultrasound (*i.e.* longitudinal pressure waves) on the chemical reactivity.

The pressure-wave intensity commonly used in sonochemistry is of the order of a few bars. Taking into account that in any liquid, even freshly distilled, there are a lot of microdust particles containing microbubbles trapped in microcrevices, a pressure wave of this intensity induces cavitation [1]. By cavitation we mean the formation, oscillation, collapse, fragmentation of bubbles in a liquid. When cavitation is caused by acoustic waves, it is called acoustic cavitation. Other kinds of cavitation are well known: the cavitation induced by a fast rotating propeller is a well-known example of hydrodynamic cavitation [2].

Homogeneous sonochemistry is referred to when the liquid phase, before sonication, is homogeneous. When the system is heterogeneous before sonication (solid suspension, two non-miscible liquids) heterogeneous sonochemistry is the term used. Homogeneous sonochemistry is the result of the extreme conditions prevailing in the collapsing cavitation bubbles. The high gas-phase temperature (a few thousand K) and the high pressure (probably a few hundred bars) at the end of the collapse [3] are sufficient to generate radicals by homolytic cleavage of gases, solvent vapor or solute vapors. At the end of the collapse, when fragmentation occurs, the radicals are injected into the bulk where they are able to react, at normal T, with molecules or other radicals. As a typical example, water is cleaved into H[•] and OH[•] radicals which subsequently can give H₂, H₂O₂ but can also recombine to give H₂O. A hot layer around the collapsing bubbles seems to be present and thermal degradation of hydrophobic molecules can take place in this region. The yield of the primary homolytic reactions taking place inside the gas phase of the collapsing bubbles is generally very poor, typically of the order of 10⁻⁵ mol/min. Of course, in some cases, the subsequent

reactions that take place in the bulk are chain reactions leading to higher yields. Homogeneous sonochemistry is essentially of real interest to physical chemists or physicists interested in what happens in a cavitating liquid [4]. The situation is dramatically different in the case of heterogeneous sonochemistry which appears to be a very useful method in synthetic organic chemistry [5]. The present paper describes a few examples of heterogeneous sonochemistry with a strong emphasis on an artifact problem which is generally underestimated or even ignored.

The Misleading Definition of a Sonochemical Effect

Classically a sonochemical effect is measured by comparing the yield of a reaction after a definite period of time in the presence (m%) and absence (n%) of ultrasound (US). If m/n is higher than 1, the reaction is said to be sensitive to US. To apply this general definition to the particular case of a heterogeneous reaction leads to difficulties. Indeed n depends on the agitation conditions and therefore the sonochemical effect m/n depends also on n.

Scheme 1. Alkaline hydrolysis of benzoate

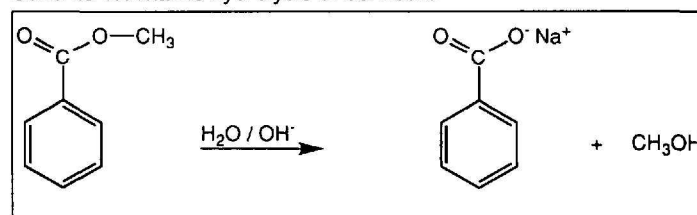


Table 1. Alkaline hydrolysis of benzoate; yields in sodium benzoate obtained under different reaction conditions (T = 40 °C, reaction time: 1 h)

Reaction conditions	Yields in sodium benzoate [%]
Magnetic agitation	0
Ultrasound	44 ± 2
UltraTurax 8000 rpm	9 ± 1
UltraTurax 16000 rpm	28 ± 2
UltraTurax 24000 rpm	33 ± 3

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Scheme 2. Cyclopropanation of cyclohexene by dichlorocarbene. Dichlorocarbene is synthesized *in situ* from chloroform and sodium hydroxide

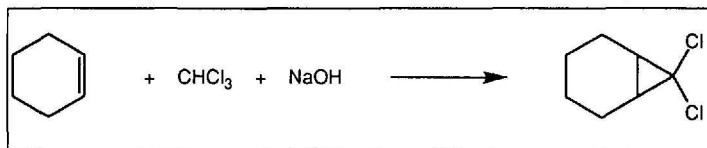


Table 2. Cyclopropanation of cyclohexene by dichlorocarbene; yields in 7,7-dichlorobicyclo[4.1.0]heptane obtained under different reaction conditions (T = 15 °C, reaction time: 4 h 30 min)

Reaction conditions	Yields in 7,7-dichlorobicyclo[4.1.0]heptane [%]
Magnetic agitation	0
Vibrating agitation	3 ± 1
Ultrasonic bath + vibrating agitation	40 ± 1
Ultrasound horn	20 ± 1
UltraTurax 8000 rpm	23 ± 6
UltraTurax 16000 rpm	53 ± 3
UltraTurax 24000 rpm	70 ± 4

For the same value of *m*, the sonochemical effect will be higher if the agitation is poor than if the agitation is efficient! Unfortunately, in the great majority of published sonochemical effects on heterogeneous reactions, the agitation conditions used to perform the so-called silent reactions were not optimized. Very generally, user-friendly but inefficient magnetic stirrers are used. As shown in Tables 1 and 2, the use of an efficient agitation system (UltraTurax with a controlled rotation rate between 8000 rpm and 24000 rpm) leads to a strong increase of *n* with respect to what is obtained with a common magnetic stirrer characterized with a rpm of the order of 1000. The exemplified reactions are the hydrolysis of methyl benzoate [6], a liquid–liquid reaction (Scheme 1, Table 1) and cyclopropanation of cyclohexene [7] (Scheme 2, Table 2), a solid–liquid reaction. Other examples have been studied leading to the same conclusions.

Even the well-known heterogeneous sonochemical switching [8][9], considered by Mason and Luche as a clear-cut proof that sonochemistry is definitively a new kind of chemistry and not ‘just another method of providing agitation of a medium’ [10], is also observed if magnetic agitation is compared to efficient agitation.

Efficient agitation with the UltraTurax leads to hydrodynamic cavitation. It could be argued that what is observed under efficient agitation is a kind of sonochemistry without sound or ultrasound or, better, another kind of cavitation chemistry.

This may be the case and work is in progress in our laboratory to determine if (or when) hydrodynamic cavitation can replace acoustic cavitation. However, as soon as *n* is agitation dependent (which is obviously the normal case) it becomes necessary to make a better definition of what a sonochemical effect is, especially in the case of heterogeneous chemistry. The previous classical definition in terms of the *m/n* ratio leads to the disastrous situation that it is impossible to differentiate fact from artifact!

The Sonoelectropulse Method for the Preparation of Fine Powders

Acoustic cavitation leads to erosion of pipes, immersion horns, vessel walls. Generally, these effects are considered as negative. Nevertheless, they can be very helpful to prepare fine powders [11–17]. The basic idea is very simple: a titanium electrode which can act also as an immersion ultrasonic horn (sonotrode) is immersed into a metallic salt solution together with the counter electrode. If the active sonoelectrode is a cathode, the reduction of the metallic ion leads to the deposition of crystalline metal on the sonoelectrode surface. If the current density is high and if the electric current is applied for a few milliseconds only, microcrystals are formed. Their size is dependent on the length of the current pulse. Then the sonoelectrode acts as a sonotrode for a few milliseconds: an intense 20 kHz pressure wave is sent through the horn into the liquid. Cavitation occurs just below the horn tip and the asymmetric implosion of cavitation bubbles leads to a cleaning of the electrode surface: the small crystals are ejected and they will never grow larger. After a waiting time of a few tenths of milliseconds necessary to refill the double layer at the surface of the electrode, a new sequence of electric pulse, acoustic pulse and waiting time starts. In this way one gram of fine metallic powder is produced in a few hours. Typically the crystal size is around 40 nm or larger depending on the length of the electric pulse. The size distribution is narrow. If the electrolytic bath contains a binary or a ternary mixture of salts, alloys are obtained with a composition which generally is similar to the bath composition. If the electrode acts as an anode, oxides can be obtained.

Table 3. Some nanopowders produced by pulsed sonoelectrolysis of aqueous salt solutions

Type of electrode	Electrolyte solvent	Ion(s) in solution	Nanoparticle composition	Reference
Cathode	Water	Cu ²⁺	Cu	[11][12]
		Co ²⁺	Co	[12]
		Zn ²⁺	Zn	[13][17]
		Cu ²⁺ + Zn ²⁺	Cu–Zn alloys	[13][17]
		Ni ²⁺	Ni	[14]
		Cr ⁶⁺	Cr	[14]
		Ag ⁺	Ag	[14]
		Cd ²⁺ + Te ⁴⁺	CdTe	[14]
		Co ²⁺ + Ni ²⁺ + Fe ²⁺	Fe–Ni–Co alloys	[15][16]
		Cathode	DMSO	Co ²⁺ + Sm ³⁺
Co ²⁺ + Gd ³⁺	Co–Gd alloys			unpublished
Anode	Water	Mn ²⁺	MnO ₂	[14]

This method seems very promising because it gives easy access to fine powders by using simple starting salts. The metallic powders are very pure and very active when, for example, they are used as reactants in organozinc chemistry [14]. The possibility to obtain alloys is also very promising. This sonoelectro-method illustrates the use of ultrasound to 'clean' the electrode surface by expelling the freshly formed solid particles. In this specific case it is difficult to imagine an other method leading to a similar 'cleaning' effect.

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Electronic Structure of Matter: Wave Functions and Density Functionals

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Traditionally, since about 1930, the electronic structure of matter has been described by Schroedinger wave functions (WF). More recently an alternative formulation known as density functional theory (DFT) has been developed, which describes electronic structure in terms of the electronic density distribution, $n(r)$. DFT was recognized by a Nobel Prize in 1998.

In this talk I have tried to convey the strengths and weaknesses of DFT in comparison with WF methods. DFT provides a new conceptual perspective on electronic structure. Its practical usefulness lies in its ability to deal with systems of O(1000) atoms compared with O(10-100) atoms for WF methods. For small systems, WF methods are more reliable and accurate.

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