



Organic reactions in water or biphasic aqueous systems under sonochemical conditions. A review on catalytic effects



Giancarlo Cravotto^{a,b,*}, Emily Borretto^a, Manuela Oliverio^c, Antonio Procopio^c, Andrea Penoni^d

^a Dipartimento di Scienza e Tecnologia del Farmaco, University of Turin, via P. Giuria 9, 10125 Torino, Italy

^b NIS-Centre for Nanostructured Interfaces and Surfaces, University of Turin, via P. Giuria 9, 10125 Torino, Italy

^c Dipartimento di Scienze della Salute, Università Magna Graecia, Viale Europa, 88100 Germaneto (CZ), Italy

^d Dipartimento di Scienza e Alta Tecnologia, University of Insubria, Via Valleggio 11, 22100 Como, Italy

ARTICLE INFO

Article history:

Received 21 September 2014

Received in revised form 6 December 2014

Accepted 16 December 2014

Available online 20 December 2014

Keywords:

Reactions in water

Aqueous biphasic systems

Heterogeneous catalysis

Ultrasound

Cavitation

ABSTRACT

Catalysis in aqueous systems under sonochemical conditions has become an irreplaceable method in green synthetic chemistry after more than two decades of studies in this domain. The present review has the aim of describing the state-of-the-art with a comprehensive view of advantages and limitations as well as new potential applications. Catalytic procedures in water assisted by ultrasound and/or hydrodynamic cavitation are environmentally friendly with milder conditions, shorter reaction times and higher yields. Sonochemical processes can reduce the formation of hazardous by-products, the generation of waste and also produce energy savings. Cavitation implosion generates mechanical and chemical effects such as cleaning of catalyst surface and formation of free radicals by sonolysis of water. The present overview of sonochemical reactions in water (oxidation, bromination, aza-Michael, C–C couplings, MCR and aldol reactions) should provide useful models for furthering the progress of organic synthesis using harmless and greener sound energy.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Ultrasound (US) and hydrodynamic cavitation (HC) have proven themselves to be an important stepping stone towards process intensification in organic synthesis, placing sonochemistry among the elite of green chemical methods [1,2]. An acoustic pressure wave consists of alternate compressions and rarefactions in the transmitting medium along the wave propagation direction. When a large negative pressure is applied to a liquid, intermolecular van der Waals forces are not strong enough to maintain cohesion and small cavities or gas-filled microbubbles are formed. The rapid nucleation, growth and collapse of these micrometer-scale bubbles constitute the phenomenon of cavitation. Sonochemical effects mainly arise from acoustic cavitation which generates enough kinetic energy to drive reactions to completion and releases short-lived, high-energy chemical species into solution after the implosive collapse of bubbles. It is now well-established that this process is capable of providing very high temperatures (4500–5000°K as typical figure) and very high pressures (≈ 1000 atm) in extremely short times (in the range of microseconds), thus rendering cavitation a quasi-adiabatic phenomenon [3]. US is especially efficient in activating hard metal surfaces as the well-known cleaning effect of ultrasonic waves provides a de-passivated layer where catalyst and reagent better interact with each other [4].

US promotes reagent diffusion from solution to the metal, electron transfer from the active surface to the reducible point of the organic substrate and finally, the extraction of ions from the surface to generate a soluble product [5]. Acoustic waves and cavitation strongly promote all these steps as observed in the formation of common organometallics under sonication [6,7]. Fig. 1 schematize the most common ultrasonic devices to work in batch with high-intensity US.

It is possible to empirically distinguish true chemical effects from mechanical ones, especially in heterogeneous reactions. In modern synthesis, so-called false sonochemistry is closely related to mechanochemistry and illustrates the advantages of using pressure waves in chemistry [8].

HC, a part of cavitation chemistry, also enables efficient catalysis under mild conditions by generating cavitation at low energy consumption. Easier scaling-up facilitates large-scale applications in several chemical processes, mainly in aqueous media such as oil hydrolysis, polymerization and depolymerization as well as oxidation reactions [9] and pollutant degradation [10]. HC use in organic synthesis and catalysis has not yet been explored as deeply as acoustic cavitation, but it is a powerful tool which has captured both academic and industrial interest [11].

Cavitation phenomena are able to dramatically enhance the reaction rates of several chemical conversions by means of mechanical effects in heterogeneous processes and chemical induction in homogeneous systems. Besides shortening reaction times and improving yields, cavitation may also induce higher selectivities while simplifying experimental

* Corresponding author at: Dipartimento di Scienza e Tecnologia del Farmaco, University of Turin, via P. Giuria 9, 10125 Torino, Italy.

E-mail address: giancarlo.cravotto@unito.it (G. Cravotto).

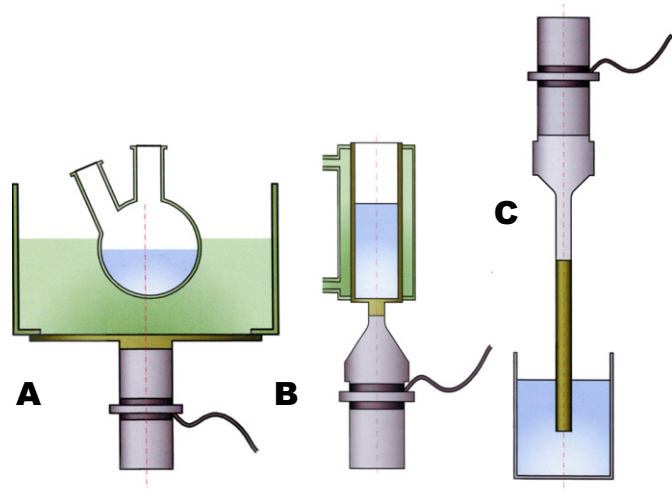


Fig. 1. US probe transducers, A) Cup horn bath, B) Cup horn cavitating tube, C) Immersion horn.

procedure and workup. Synthetic protocols involving metal catalysis have long been a favorite and most rewarding topic in sonochemistry. The majority of such studies have focused on heterogeneous reactions performed in water or aqueous media [12], considered the solvent of choice in sonochemistry thanks to the excellent cavitation it facilitates from room temperature up to 50–60 °C. Besides being inexpensive, abundant, non-toxic and environmentally friendly, water can also be used as a dispersing medium under US. In addition to satisfying the above criteria, water also causes special effects in reactions that arise from intra- and inter-molecular non-covalent interactions and which lead to assembly processes.

As stated by Sheldon (1996), in green procedures “The best solvent is no solvent and if a solvent (diluent) is needed it should preferably be water” [13]. Sonochemical reactions in water often bring to the fore peculiar reactivities and selectivities that are not observed under anhydrous conditions [14]. In this respect, the development of water-tolerant catalysts and reagents has rapidly become an area of intense research.

One of the main limitations in the scale up of sonochemical equipment is the energy consumption. The flow and loop US reactors stand out above classic batch US reactors thanks to their greater efficiency and flexibility as well as lower energy consumption. Fig. 2 shows a multi-horn flow reactor in which the reacting mixture is pumped through the system.

2. Use of surfactants

Organic reactions in water are often difficult because most organic reactants, including catalysts, are insoluble in water. Surfactants, due to their dual hydrophobic and hydrophilic nature, can ride out this problem by forming micelles and promoting reactions in water. An example is *p*-dodecyl-benzenesulfonic acid (DBSA), a Brønsted acid-surfactant that combines catalytic action and the ability to form stable colloidal dispersions with water-insoluble substrates that facilitate reaction outcome. Proton acid catalyzed organic reactions can be carried out in the presence of water using DBSA [15]. It has been widely reported that US, when compared with conventional protocols, accelerates reactions via a more intimate mixing of reagents and enhances the activity of an insoluble catalyst by enlarging its surface area [16]. Li et al. reported two examples of improvements in organic syntheses in water via the use of DBSA under US. Firstly [17], they reported a green, efficient procedure for the preparation of *bis*(indolyl)methanes from indole and aromatic aldehyde in the presence of DBSA in aqueous solution (Scheme 1).

The same group reported the DBSA catalyzed synthesis of amidino-hydrazones under US in water. These versatile synthetic intermediates

were obtained via the condensation of 1,5-diaryl-1,4-pentadiene-3-ones with aminoguanidine hydrochloride [15] (Scheme 2).

The nucleophilic attack of the amino group to the carbonyl is followed by water elimination and DBSA catalysis is important in creating a good leaving group. The condensation of the solid–liquid mixture is strongly promoted by the emulsification generated by US in the presence of DBSA that increase the interfacial contact area of the reagents. The comparison between US and simple stirring reported in Table 1 evidenced the advantages of sonochemical catalysis, with shorter reaction times and higher yields.

Li et al. [18] reported a simple, efficient procedure for the deoxygenation of keto- and aldoximes to the corresponding carbonyl compounds using silica sulfuric acid/paraformaldehyde in water in the presence of sodium dodecylsulfonate (SDS) under US. The formation of ketones and aldehydes from oximes is useful because oxime serves as an efficient protective group for carbonyls, which are extensively used for the purification of carbonyl compounds. A typical deoxygenation protocol requires harsh conditions and reagents, sustained heating under reflux, a tedious work-up and may generate side products. Silica sulfuric acid is an excellent candidate for sulfuric acid or chlorosulfonic acid replacement in organic reactions and does not entail limitations such as the destruction of acid sensitive functional groups, the use of rather toxic solvents and expensive reagents (Scheme 3).

Sonochemical deoxygenation reactions were carried out on aldoximes in good yields using silica sulfuric acid in the presence of SDS. Experiments carried out under silent conditions gave comparable yields but in a much longer reaction times. The various substituents on the benzene ring affect product yield. When ketoximes that contain electron-donating groups on the benzene ring were used as substrates, ketones were obtained in good yields (92–97%), whereas ketoxime containing electron-withdrawing group gave the ketones in about an 80% yield. In addition, the catalyst can be reused three times without significant decrease in activity. It is worth noting that no Beckmann rearrangement products were formed.

3. Small catalyst molecules

Organic reactions catalyzed by small organic molecules have drawn a great deal of attention. Urea derivatives may coordinate carbonyl groups

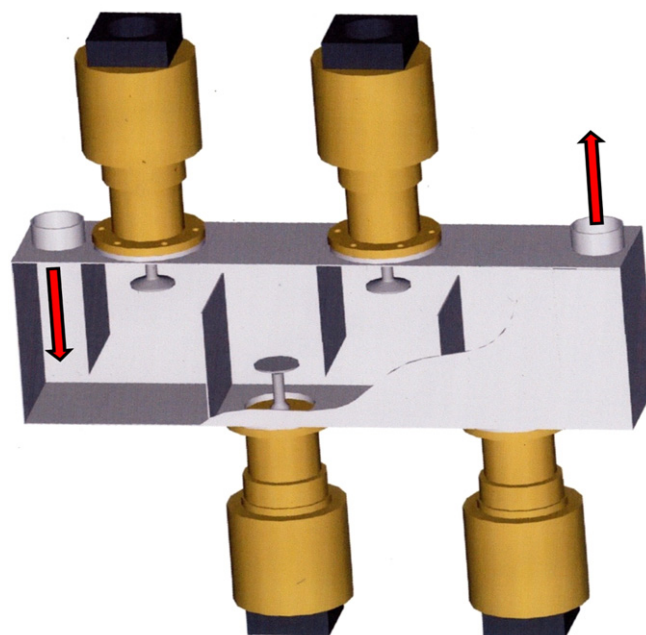


Fig. 2. Multi-horn flow reactor (developed at the University of Turin in collaboration with Danacamerini sa.).

Download English Version:

<https://daneshyari.com/en/article/50353>

Download Persian Version:

<https://daneshyari.com/article/50353>

[Daneshyari.com](https://daneshyari.com)