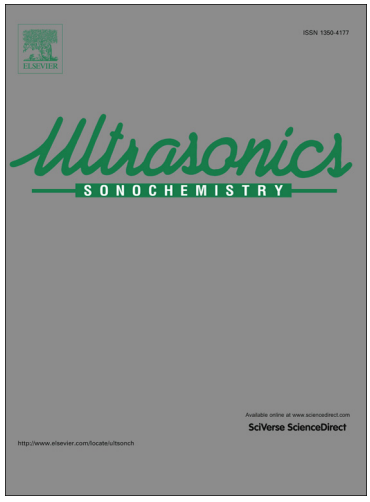

Non-innocent probes in direct sonication: Metal assistance in oxidative radical C-H functionalization

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Non-innocent probes in direct sonication: Metal assistance in oxidative radical C-H functionalization

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Abstract

Direct sonication by means of ultrasound horns constitutes a widely used technique in chemical process technology. However, the direct contact between the metal probe and the reaction mixture does not always leave the chemical system unaffected. In this report, we study the *tert*-butyl hydroperoxide-mediated trifluoromethylation of heterocyclic structures, and the influence of sonication thereon. Metal leaching is observed during the process and further examined, showing that several metals can interfere significantly with the chemical reaction under study. Notably, vanadium metal was found to increase the reaction rate exceptionally well, rendering it a useful additive for this type of reactions. Ultimately, some mechanistic considerations are offered, to provide more insight into the nature of the catalytic effect of leached metals.

Keywords: ultrasound horn – corrosion – vanadium – Minisci reaction – sonochemistry – radical chemistry

1. Introduction

Ultrasonic irradiation has proven to be a valuable, non-conventional energy source in organic synthesis [1-4]. By merit of rarefaction-compression cycles and the subsequent formation and implosion of gas-filled or vacuum cavitations, local hot spots are formed with very high local temperatures and pressures (up to 5000K and > 500 atm) [5,6]. These cavitations can serve as microreactors, wherein compounds either react inside the bubble, or on the boundary upon implosion. Especially noteworthy about the cavitation phenomenon is the formation of all kinds of radicals inside the bubble, due to homolytic cleavage of e.g. O-H bonds in water molecules [7,8].

Another benefit of ultrasonication is its ability to replace phase transfer catalysis, as it allows for more efficient micromixing than conventional stirring [9,10]. Also, near solid surfaces, the implosion of a bubble will act as a microjet towards the surface and thus by causing structural defects it will enlarge the specific surface area of the solid [11,12].

From a processing point of view, it was hypothesized by Gogate that ultrasound (US) irradiation can assist chemical reactions in seven ways: (a) reaction time reduction (b) increase in the reaction yield (c) use of less forcing conditions (temperature and pressure) as compared to the conventional routes (d) reduction in the induction period of the desired reaction (e) possible switching of the reaction pathways resulting in increased selectivity (f) increasing the effectiveness of the catalyst used in the reaction (g) initiation of the chemical reaction due to generation of highly reactive free radicals [13].

In its most accessible form, and therefore particularly interesting for lab-scale applications, ultrasound irradiation can be generated with an ultrasound horn. In this user-friendly, compact enough device, a piezoceramic element brings about the acoustic waves incited by a processor, and a cylindrical sonotrode or ‘horn’ to which it is connected can transmit the vibrations to a certain medium. Vertically positioned, the tip of the horn will usually be immersed between 1 and 3 cm in the fluid, in the center of the vessel. Its ease of use allows the researcher to rapidly assemble a set-up for sonication experiments, without the need for reactor design etc. as one would have to do with indirect sonication methods. As compared to the ubiquitous ultrasonic cleaning baths, which are plagued by low power densities and inhomogeneous US fields, the probe can provide local intensities of several orders of magnitude higher [14].