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Sonication effects on non-radical reactions. A sonochemistry beyond the cavitation?

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ABSTRACT

The kinetics of pH-independent hydrolysis of 4-methoxyphenyl dichloroacetate were investigated under ultrasonic irradiation with an application of 10% of the maximum power of the equipment and without sonication in acetonitrile–water binary mixtures with a content of acetonitrile ranging from 0.008 to 35 wt.%. Similar kinetic investigations were performed at intensities corresponding to 10%, 20%, 30%, 40%, and 50% of the input energy in solvent mixtures containing 10 wt.% and 25 wt.% acetonitrile. In parallel, the responses of KI and terephthalic acid dosimeters at applied irradiation levels were registered under the same experimental conditions. Significant kinetic sonication effects were found at sound intensities presumably not inducing cavitation in the solution. This result provides an experimental evidence of kinetic effects of ultrasound in the absence of cavitation. A disturbing impact of cavitation on the ultrasonic acceleration of the reaction was found. The implications of these findings were discussed.

1. Introduction

Sonochemical reactions in solutions have mainly been rationalised in terms of cavitation theory, assuming that the sonication effects are connected with the formation of cavitation bubbles [1–4] acting as closed microreactors and having interior environmental conditions different from those in the bulk liquid phase [5]. For example, solvents can be vaporised into the bubble and undergo pyrolytic cleavage to form radicals or excited chemical species, which in turn may induce subsequent reactions with less volatile substrates. Certainly, the latter processes may also occur on the bubble shell or even be transferred into the bulk medium, but the nature of the chemical process should remain unchanged. Following this idea, a rule was formulated by Luche [4] that homogeneous reactions activated by sonication should proceed exclusively via radical or radical-ion intermediates, and ionic reactions which cannot be switched to a radical pathway should not be susceptible to ultrasound. However, numerous examples of homogeneous reactions which definitely proceed from non-radical mechanism have been found to be accelerated by ultrasound [6–8].

The mode of action of ultrasound on reactions in solutions has been discussed proceeding from the number of cavitational sites generated by irradiation in the reaction medium [6–10]. It appears that just 0.1% or even less of the reaction medium can simultaneously be under cavitation [9]. If the reaction occurred exclusively in the cavitational sites, the ultrasonic acceleration effect would have to be about 10^3 times or even more to produce the observed rate enhancement by a factor of two. In other words, the reaction localized in the cavitational sites has to proceed several thousand times faster than in the bulk solution. Such rate enhancement seems inconceivably high for any of the ionic reactions sonochemically investigated to date. As such, the observed acceleration of polar homogeneous reactions cannot be presented as a phenomenon that should be exclusively located in the cavitation bubbles.

Another intriguing issue addressed previously was the direction of the ultrasound effect on the reaction rate. Classical cavitation theory predicts only ultrasonic acceleration [1–4]. However, it was found that in the presence of ultrasonic radiation the reaction of benzoin condensation of benzaldehyde was slowed by 20% [10,11]. This retardation effect was most pronounced in pure water and was gradually decreased with increasing ethanol content in the solution. Most interestingly, the possibility of ultrasonic retardation of chemical reactions was predicted as early as in 1997 [12] and its discovery provided direct and unambiguous evidence of the need to extend and advance the principles of sonochemical theory.

The initial understanding for this advancement could be the fact that the translational energy of species (accordingly, the effective temperature of species) can be affected by sound waves passing through the medium, and this rather modest energy should be sufficient to change the reaction rate [13]. Apart from the kinetic effects observed in the case of ionic reactions, the acoustically induced motion of water of crystallisation has been observed, leading to changes in the melting points of compounds [14]. The perturbations of normal molecular motion in the liquid phase as well as conformational changes to the constituent molecules of the sample

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induced by ultrasound have also been detected in NMR spectra [14–16]. It has been accepted that equilibria involving aggregates present in the solution are perturbed by pressure changes produced by sound waves [17] and that relaxation processes in liquids are caused by the reestablishment of the equilibria that have shifted in the acoustic field [18,19]. It was recently found that in the absence of cavitation, ultrasound can increase the nucleation temperature of ice in water [20]. All of these data point to the possibility that different complex formation phenomena may be practically affected by moderate acoustic energy.

In this context works by the Moholkar group ([21–24] and Refs. therein) deserve serious attention. Besides application of ultrasound to solve different technical and environmental problems, the authors have made an attempt to link up the sonochemistry with sonophysics with simulations of cavitation bubble dynamics for different chemical systems. Most important, they showed the distinctive effect of cavitation as isolated from the joint effect of ultrasound and cavitation. In this way the authors introduced discernment between the effects caused by plain propagation of ultrasound and by cavitation phenomena in the medium. Most recent publications by the group deal with both physical [21,22] and chemical [23,24] effects.

Our former kinetic data obtained for reactions in solutions did not permit true acoustic field effects to be discerned from those caused by pressure waves due to cavitation phenomena. This is because we have assigned the observed kinetic sonication effects to cavitation or to shock waves produced by it [6–9]. However, in this work we present an experimental evidence of the kinetic effects of ultrasound in the absence of cavitation.

The pH-independent hydrolysis of 4-methoxyphenyl dichloroacetate in acetonitrile–water binary mixtures was taken under consideration. The kinetic effects of irradiation with ultrasound of varying power were contrasted with dosimetric data determined under the same conditions. It appeared that the kinetic effects of ultrasound were present at sound intensities presumably incapable of inducing cavitation in the solution. The implications of this finding were discussed in the work.

2. Experiments

2.1. Reagents and solvents

4-Methoxyphenyl dichloroacetate was prepared according to literature [25]. The 4-methoxyphenol (4-MP) and the starting materials for the synthesis of the ester, as well as all of the reagents used for dosimetries, were purchased from Aldrich and were used as received.

All of the solutions were made up by weight using Millipore Milli-Q water. The acetonitrile was of analytical grade (Aldrich).

2.2. Apparatus

All of the kinetic and dosimetry experiments were conducted in a flat-bottomed cylindrical reaction vessel (internal diameter = 46.5 mm) using the online system developed for kinetic measurements under ultrasound [26]. According to the experimental requirements, either a UV/Vis detector (Shimadzu SPD-20A, SHIMADZU CORPORATION, Kyoto, Japan) or a fluorescence detector (Gilson, Model 121, GILSON MEDICAL ELECTRONICS, Inc, Middleton, USA) were used. Ultrasound was generated using an Elma TI-H-5 MF2 (Elma Hans Schmidbauer GmbH & Co. KG, Singen, Germany) cleaning bath operated at 25 kHz (nominal power 100 W). The temperatures in both the reaction vessel and the ultrasonic bath were maintained at 25.0 ± 0.1 °C for all experiments, controlled with a Refrigerated Heating Circulator Bath (Ministat 125, Peter Huber Kältemaschinenbau GmbH, Offenburg, Germany). According to the calorimetric measurements carried out in the reaction vessel, the ultrasonic power of the cleaning bath adjusted to 50% of the input energy was equivalent to 1.6 ± 0.5 W/150 mL in water.

2.3. Kinetic measurements

Kinetic measurements of the pH-independent hydrolysis of the 4-methoxyphenyl dichloroacetate were carried out with and without sonication in 0.008–35 wt.% aqueous acetonitrile. An argon atmosphere was applied to prevent oxidation of reagents by air. The pH of all solutions was adjusted to 3.6 (using aqueous HCl) to keep the reaction in the region of the pH-independence (pH from 1.5 to 6.0 as determined in this work).

For kinetic measurements under ultrasound, 150 mL of the water–acetonitrile solvent mixtures were transferred to the reaction vessel. The ultrasound was switched on and the power of the cleaning bath was adjusted. Once thermal equilibrium was obtained, 10 μL of the acetonitrile solution of the calculated amount of 4-methoxyphenyl dichloroacetate was injected into the reaction cell, providing a 10^{-5} M initial concentration of the ester. The kinetics was followed at the wavelength of maximum absorption of 4-methoxyphenol (290 nm). Pseudo-first-order rate constants were calculated by means of a differential method. All non-irradiated kinetic runs were performed similarly using the same equipment. At least duplicate kinetic runs showed the average reproducibility within 4–7%.

2.4. Degradation of 4-methoxyphenol (4-MP)

The sonolytic degradation of 4-MP was monitored under the same conditions as the hydrolysis of 4-methoxyphenyl dichloroacetate. Experiments were carried out in 10 wt.% acetonitrile–water mixtures with a 10^{-5} M initial concentration of 4-MP. Kinetic measurements were performed at different intensities corresponding to 10%, 20%, 30%, 40% and 50% of the input energy of the cleaning bath. Measurement period was 60 min. The first-order degradation process was followed spectrophotometrically observing the change in absorption at 290 nm.

The rate constant of the sonolytic degradation of 4-MP was found to be $k = 2.19 \times 10^{-6}\ s^{-1}$ in the case of 50% of electrical input energy while the corresponding rate constant of the ester hydrolysis was $k = 1.05 \times 10^{-3}\ s^{-1}$ under the same conditions [27]. No degradation of the 4-MP was detected during the one hour of sonication with ultrasonic power adjusted at 10% and 20% of electrical input energy.

2.5. Dosimetry

Potassium iodide (KI) and terephthalic acid (TA) dosimetry reactions were carried out at irradiation intensities corresponding to 7%, 10%, 20%, 30%, 40% and 50% of the input energy of the ultrasonic bath under the same experimental conditions as the kinetic measurements using the online spectrometric system [26] (Section 2.2).

KI dosimetry was performed with a solution of 0.1 M potassium iodide (KI) prepared in a 10 wt.% acetonitrile–water solvent mixture. To enhance the oxidation of iodide [28], a few drops of carbon tetrachloride were added to 150 mL of KI solution in the reaction vessel. The formation of I_3^- was monitored at 355 nm (molar absorptivity $\varepsilon = 26{,}300\ dm^3\ mol^{-1}\ cm^{-1}$ from calibration) with a UV/Vis detector (Section 2.2). KI dosimetry measurements were performed for each applied irradiation level in at least two independent runs with a reproducibility of ±4%.