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Sonolysis of Aqueous Solutions under Argon: Dependence of the Rate of Hydrogen Peroxide Formation on Hydroxyl Radical Scavenger Concentration

Dmitrii N. Rassokhin,* Mikhail B. Gokzhaev, Lenar T. Bugaenko and Georgii V. Kovalev

Department of Chemistry, M. V. Lomonosov Moscow State University, 119899 Moscow, Russian Federation.
Fax: +7 095 939 3952; E-mail: TSIR@elch.chem.msu.su

The dependence of the rate of formation of hydrogen peroxide on $^{\bullet}OH$ radical scavenger concentration in aqueous solutions exposed to ultrasonic irradiation under an argon atmosphere has been investigated, and it is shown that for the scavengers used (methanol, ethanol and acetate ion) the rate decreases directly with the cube root of the scavenger concentration, analogously to the dependence observed in the radiolysis.

The mechanism of the sonolysis of water has long drawn the attention of many researchers.[1–3] It has been shown that the final products of the sonolysis of water under a noble gas atmosphere are hydrogen peroxide, molecular hydrogen and oxygen, $^{\bullet}OH$ radical and H atom being the main primary products. It is suggested that the primary products arise inside the cavitation bubbles from the decomposition of vapours and gases which flood the bubbles, either due to electrical discharge[4] or to pyrolysis, since adiabatic compression of the gas in the bubbles takes place when they collapse.[5] Unfortunately, there is no way to directly observe the sonolytic intermediates, as is the case in radiation chemistry using the pulse radiolysis method.[6] For the time being, the only direct method is the observation of sonoluminescence spectra and the timing of the sonoluminescence flash;[1,2,7] this allows the recognition of the existence of some excited particles in the plasma inside the cavitation bubbles (for instance C_2* has been found in the sonolysis of silicone oil). It does not, however, provide data on the spatial distribution and transformations of short-lived radical intermediates. In radiation chemistry before the pulse radiolysis method was elaborated many researchers had been using a scavenger method to study reactions with the participation of non-directly observable intermediates.[8] This scavenger method allows for the elucidation of the nature of the final product precursors, their concentrations and, in some cases, their spatial distribution from the influence of various added substances (referred to as scavengers), capable of reacting with the radicals, on the rate of formation of the final products of radiolysis. Assuming a certain similarity between sonolysis and radiolysis (see, for example, the review monograph by El'piner[1] and review article by Riesz and Kondo[3]), sonochemists have already used various radical scavengers for a study of the sonolysis of aqueous solutions,[9,10] although the dependence of the final product formation rate on the scavenger concentration has not been examined in detail. In the present study, the concentration affect of three $^{\bullet}OH$ radical scavengers (acetate ion, methanol and ethanol) on the rate of formation of hydrogen peroxide in the sonolysis of aqueous solutions has been investigated.

Sonolysis of aqueous solutions containing the hydroxyl radical scavengers was carried out at 30 °C in a special thermostated cell, ensuring the passage of the ultrasound beam through the solution without the formation of standing waves, thereby resulting in constant sonolysis parameters. The temperature of the cell was measured with a thermocouple. The ultrasonic frequency used was 724 kHz and the acoustic power output (as measured calorimetrically) was 40 W. The total volume of the cell was 100 ml, while the volume of the sample being sonicated was 50 ml. The samples were vigorously bubbled with an argon flow for 20 min before sonication. During sonication 4–6 samples of the solution were drawn from the cell for analysis. Withdrawing the samples decreases the volume of the solution; however, this did not lead to an increase in the rate of the sonochemical reactions since the height of the solution layer being sonicated decreased proportionally with a decrease in the solution volume in the cell. The concentration of hydrogen peroxide was measured spectrophotometrically using the reaction of H_2O_2 with titanyl ion in the presence of sulfuric acid giving a yellow-coloured product ($\lambda_{max} = 405$ nm, $\varepsilon = 667$ M^{-1} cm^{-1}).[†]

For different concentrations of each scavenger the curve of hydrogen peroxide concentration *vs.* sonication time was obtained, the total sonication time of each sample being in the range 6–24 min. In all cases, the curves turned out to be almost linear with an accuracy of 10%. From these curves the formation

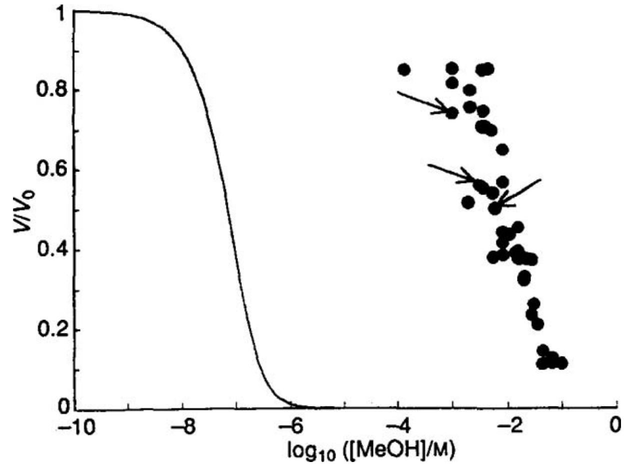

Fig. 1 The theoretical [computed from equation (3)] and experimental dependences of the relative rate of hydrogen peroxide formation on the concentration of methanol in the sonolysis of aqueous solutions. The arrows indicate the points corresponding to the data from ref. 10. ● experimental, – computed.

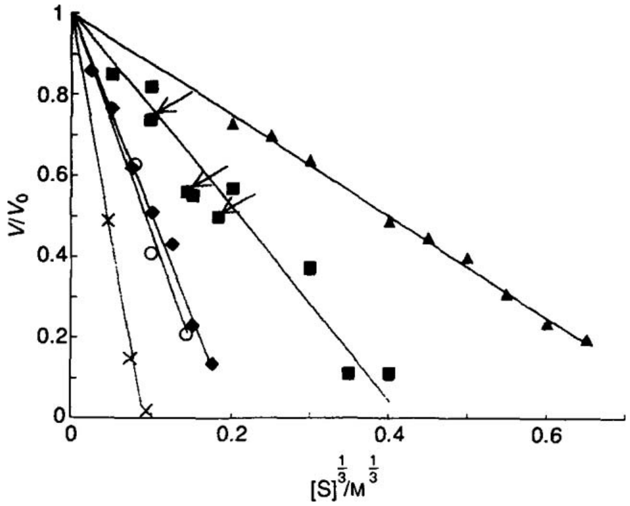

Fig. 2 The rate of hydrogen peroxide formation in the sonolysis of aqueous solutions as a function of the cube root of the •OH scavenger concentration. The data for *tert*-butanol and dioxane and the data for methanol to which the points indicated by the arrows correspond are taken from ref. 10. ◆ EtOH, ■ MeOH, ▲ acetate, × *tert*-butanol, ○ dioxane.

rates of hydrogen peroxide (V) were computed using the least-square method. As one might expect, the increase in the scavenger concentration decreased V. The data for the scavenger concentration dependence of V taken from one set of experiments fell on a smooth curve; the sets of experiments carried out at different times gave slightly differing results (within the range of 20%).

Fig. 1 shows a plot of the relative rate of hydrogen peroxide formation V/V_0, where V_0 is the rate in the absence of the scavenger [which was measured to be 1.2×10^{-3} M h^{-1} (3.3×10^{-7} M s^{-1}) under our experimental conditions] *vs.* the decimal (base 10) logarithm of the methanol concentration. Similar curves were also observed for ethanol and potassium acetate. The data from ref. 10, which was obtained by Henglein and Kormann for the sonolysis of aqueous methanol solution by 300 k Hz ultrasound, are also plotted in Fig. 1, from which we notice that those data agree well with our own data.

Formation of hydrogen peroxide in the sonolysis under an argon atmosphere is accounted for by the recombination of a pair of hydroxyl radicals, reaction (1):[1–3]

$$^\bullet\mathrm{OH} + {}^\bullet\mathrm{OH} \rightarrow \mathrm{H_2O_2} \qquad (1)$$

Scavenging of •OH radicals by the scavenger S competes with the recombination (1), reaction (2).

$$\mathrm{S} + {}^\bullet\mathrm{OH} \rightarrow \text{Products} \qquad (2)$$

Assuming a homogeneous spatial distribution of the radicals, from the condition of steady-state •OH concentration (*i.e.*, d[•OH]/dt = 0) we observe the following equation for the rate of formation of hydrogen peroxide, equation (3),

$$V = \frac{k_s^2[\mathrm{S}]^2}{16k_R}\cdot\left(\sqrt{1+\frac{8V_{\mathrm{OH}}k_R}{k_s^2[\mathrm{S}]^2}}-1\right)^2 \qquad (3)$$

where V_{OH} is the rate of •OH radical formation (which can be estimated from the rate of hydrogen peroxide formation in the absence of the scavenger: $V_{\mathrm{OH}} \approx 2V_0$); K_R is the rate constant for •OH recombination (1); and k_s is the rate constant for scavenging (2); values for those are known from the literature data[11] (5.3×10^9 and 8.4×10^8 M^{-1}s^{-1} for the recombination and scavenging by methanol, respectively). The rate of hydrogen peroxide formation computed from equation (3) as a function of methanol concentration is also shown in Fig. 1. It is clear from Fig. 1 that if the spatial distribution of •OH radicals were homogeneous, hydrogen peroxide could not arise in an analysable concentration at all concentrations of methanol used in the experiment. Similar curves are also obtained for ethanol and potassium acetate. A considerable discrepancy between the values estimated with equation (3) and those observed experimentally leads to the conclusion that there is a non-homogeneous primary spatial distribution of •OH radicals.

In radiation chemistry of aqueous solutions the problem of non-homogeneous initial spatial distribution of radicals has been considered in detail.[12,13] Under the influence of ionising radiation the radicals appear in the ionising particle tracks at concentrations of hundredths of M, that leads to the high efficiency of their recombination, even in the presence of sufficiently high scavenger concentrations. Heterogeneous spatial distribution of the radicals in the radiolysis, as shown by Byakov and Nichiporov,[12] leads to the following dependence of the rate of the formation of hydrogen peroxide on the •OH scavenger concentration, appropriate over a certain range of scavenger concentrations, equation (4),

$$V/V_0 = 1 - qc^{1/3} \qquad (4)$$

where q is the coefficient related to the reactivity of the scavenger, quantity of the radicals in the track and their spatial distribution. In the case of sonolysis, the radicals generated in the cavitation bubbles pass into the interfacial region of the solution,[3] where they enter into recombination reactions and into reactions with scavengers dissolved in the water (note that in the gaseous phase inside the cavitation bubbles a non-homogeneous spatial distribution cannot appear because of the very high diffusion coefficients of the particles). Hence, the cavitation bubbles in the sonolysis can be considered to be analogous to the ionising particle tracks in the radiolysis. Consequently, it makes sense to draw on equation (4) to fit the experimental data provided by the experiments on sonolysis. As can be seen from Fig. 2, equation (4) adequately represents the scavenger concentration dependences of the hydrogen peroxide formation rate for the three scavengers used in our experiment, as well as for the *tert*-butanol and dioxane, the data on the latter two being taken from the study by Henglein and Kormann.[10]

Thus, the data on the suppression of hydrogen peroxide formation by the scavengers of •OH radical scavengers in the sonolysis bears witness to the non-homogeneous initial spatial distribution of •OH radicals in the solution being sonicated.

A non-homogeneous initial distribution of the primary sonolysis products seems to be obvious due to the existence of the bubble-solution interface, and so, is implied by sonochemists. It is the recognition of the linear relationship between the rate of formation of the recombination product and the cube root of the radical scavenger concentration in the sonolysis that opens up a way of studying the nature of the spatial distribution of the radicals, through finding a correlation between coefficient q in equation (4) and the physical and chemical properties of the radical scavengers and sonolysis conditions, such as ultrasound irradiation parameters.

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