5aPA5. Free radical formation and scavenging by solutes in the sonolysis of aqueous solutions

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It has long been known that the primary radicals generated in water (\(\cdot H\) and \(\cdot OH\)), on the collapse of acoustic bubbles, largely recombine. It has been estimated that as much as 90% react within the bubble to produce molecular hydrogen, hydrogen peroxide and water[1]. This high recombination efficiency has been likened to radicals reacting within "spurs" produced by ionizing radiation in water. Several studies have shown that by using high concentrations (100s of mM) of primary radical scavengers, e.g., aliphatic alcohols, iodide, etc., a large number of the primary radicals are able to be captured in acoustically produced hot spot spurs. What is less well examined is the effect the scavengers themselves have on the production of the primary radicals and hence on the radical yields measured. The talk will consider the effect that typical radical scavengers have on active bubble populations in aqueous solutions, and on the production of primary radicals in the presence of added solutes. I. A. Henglein, Ultrason. Sonochim. 2, S115-S121 (1995)

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FREE RADICAL FORMATION AND SCAVENGING BY SOLUTES IN THE SONOLYSIS OF AQUEOUS SOLUTIONS

During the sonolysis of argon saturated water the primary sonochemical reaction to occur is the thermolysis of water molecules within cavitation hot spots, as can be represented by reaction 1.\(^1\)

\[
\text{H}_2\text{O} \xrightarrow{\text{leading}} \cdot\text{OH} + \cdot\text{H} \quad \ldots(1)
\]

The primary radicals \(\cdot\text{H}\) and \(\cdot\text{OH}\) have been found to largely recombine (about 80 to 90\%) within the cavitation to regenerate water, or to form \(\text{H}_2\) and hydrogen peroxide. Of these reactions the dominated one is the recombination step producing water (about 80\%).\(^2,3\)

In order to make the maximum use of the primary radicals, with respect to initiating chemical reactions in a sonochemical system, radical scavengers are needed in order to prevent the recombination processes. Aliphatic alcohols are known scavengers of both \(\cdot\text{H}\) and \(\cdot\text{OH}\) and have been commonly used in radiation chemistry studies for exactly that purpose.\(^4,6\) The corresponding reactions can be generically described as,

\[
\text{RHOH} + \cdot\text{OH}/\cdot\text{H} \rightarrow \cdot\text{ROH} + \text{H}_2\text{O}/\text{H}_2 \quad \ldots(2)
\]

The alcohol radicals (\(\cdot\text{ROH}\)) are relatively strong reductants and can be readily detected by their reaction with a good electron acceptor, e.g., Fe(CN)\(_6\)^{3−}. A specific and well-studied reaction sequence is,

\[
(\text{CH}_3)_2\text{CHOH} + \cdot\text{OH} \rightarrow (\text{CH}_3)_2\text{COH}^+ + \text{H}_2\text{O} \quad \ldots(3)
\]

with \(k_3 = 2 \times 10^9\text{ M}^{-1}\text{s}^{-1}\)

\[
(\text{CH}_3)_2\text{COH}^+ + \text{Fe(CN)}^\text{6}^{3−} \rightarrow (\text{CH}_3)_2\text{CO} + \text{Fe(CN)}^\text{6}^{4+} + \text{H}^+ \quad \ldots(4)
\]

with \(k_4 = 4 \times 10^9\text{ M}^{-1}\text{s}^{-1}\)

Hydrogen abstraction from iso-propyl alcohol (IPA) in reaction (3) is quite specific with about 85\% of the \(\alpha\)-radical being produced as shown.\(^5\) Similarly, the \(\cdot\text{H}\) reactions of relevance are,

\[
(\text{CH}_3)_2\text{CHOH} + \cdot\text{H} \rightarrow (\text{CH}_3)_2\text{COH}^+ + \text{H}_2 \quad \ldots(5)
\]

with \(k_5 = 7.4 \times 10^7\text{ M}^{-1}\text{s}^{-1}\)

\[
\cdot\text{H} + \text{Fe(CN)}^\text{6}^{3−} \rightarrow \text{Fe(CN)}^\text{6}^{4+} + \text{H}^+ \quad \ldots(6)
\]

with \(k_6 = 6.3 \times 10^9\text{ M}^{-1}\text{s}^{-1}\)

Using IPA as an \(\cdot\text{H}\) and \(\cdot\text{OH}\) radical scavenger in a sonochemical system, in principle, should be similar to what has been measured in radiation chemistry studies. Its ability to react with OH radicals produced in the sonolysis of aqueous alcohol solutions can be gauged by measurement of the hydrogen peroxide yield as a function IPA content. This is shown in Figure 1.
FIGURE 1. The rate of production of H₂O₂ as a function of IPA concentration in argon-saturated alcohol solutions sonicated using 355 kHz ultrasound. (The line drawn is to emphasis the trend).

The trend shown in Figure 1 is consistent with the IPA scavenging OH and therefore preventing hydrogen peroxide formation. However, it is known that short alkyl chain alcohols can evaporate into cavitation bubbles and reduce the hot spot temperature. In effect, also reducing the amount of thermolysis of water within the bubble and thereby hydrogen peroxide formation. In order to confirm that the IPA is acting as an ·H and ·OH scavenger the reduction of ferricyanide needs to be monitored. These measurements are shown in Figure 2.

FIGURE 2. The rate of reduction of ferricyanide as a function of IPA concentration in argon-saturated alcohol solutions sonicated using 355 kHz ultrasound. The initial concentration of ferricyanide was 1.8 mM. (From other experiments it was found that a ferricyanide concentration of 1.8 mM was sufficient to scavenge all alkyl radicals produced in the sonolysis system). (The line drawn is to emphasis the trend).

The form of the increasing rate of reduction of ferricyanide with increasing IPA concentration displayed in Figure 2 is at considerable odds with the trend seen in the decline in the rate of H₂O₂ production over the IPA concentration range used. There are several clear differences. The first is that there is an initial rate of reduction of ferricyanide at [IPA] = 0. This can be understood if this onset reduction rate is assigned to reaction 6. Secondly, the maximum rate of reduction of 2.6 ± 0.2 µM min⁻¹ is considerably smaller than the maximum rate of H₂O₂...
production \(8.4 \pm 0.2 \ \mu\text{M min}^{-1}\). In fact, based on the stoichiometry of the reactions involved where 2 moles of the isopropyl radical are formed for every mole of hydrogen peroxide not formed, the expected maximum rate of reduction of ferricyanide should be \(>16.8 \ \mu\text{M min}^{-1}\). (The greater than twice the maximum peroxide rate comes about because reaction 5 can also be expected to contribute to the formation of IPA radicals and hence reduction of ferricyanide). Lastly, the most striking difference in the two sets of data rest with the widely different concentration ranges over which the changes in the formation/reduction rates take place. It can be seen that 1 mM of IPA is sufficient to completely eliminate \(\text{H}_2\text{O}_2\) formation. However, the rate of reduction of ferricyanide continues to increase up to about 200 mM.

The most plausible explanation for the apparent contradictory results in the two sets of data is that alcohol does not act as a simple radical scavenger in the sonochemical system, but produces radicals in a separate process. Figure 3 is a pictorial representation of how this could occur. It shows a bubble expanding with adsorbed alcohol at the bubble solution interface being drawn into bubble due to the partial vacuum created on its expansion. On inertial collapse of the bubble the hot spot conditions created can be expected to dissociate trapped alcohol molecules as evidenced by the range of hydrocarbon products produced from the sonication of aqueous alcohol solutions.\(^8,9\) These hydrocarbon radicals, many known to be good reductants, may then act to reduce ferricyanide ions in solution.

**FIGURE 3.** Pictorial representation of an acoustic bubble in an aqueous alcohol solution undergoing expansion and inertial collapse to generate a hot spot. The diagram shows alcohol and water molecules evaporating into the bubble during its expansion phase and their subsequent thermolysis on bubble collapse. The radicals generated from the decomposition of the alcohol molecules subsequently react with oxidants in bulk solution.

The main conclusion that can be drawn from the study is that in an aqueous sonochemical system containing volatile alcohols, aliphatic alcohols no longer act as simple primary radical scavengers as seen in radiation chemistry studies. Their presence generates other reducing radicals and these dominate the reduction reactions that may ensue.

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**REFERENCES**