Evidence Against the Formation of Hydrated Electrons as Principal Species in the Sonochemistry of Neutral Aqueous Solutions.

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ABSTRACT.

In this work we use a sensitive method for detecting the presence of hydrated electrons in argon-saturated water exposed to 50 kHz ultrasound. This method is based on the fact that hydrated electrons, but not hydrogen atoms, can be scavenged by Cd\textsuperscript{2+} to prevent their reaction with the nitrone spin trap \textalpha-(4-pyridyl-1-oxide)-N-t-butylnitron (POBN) to form the EPR-detectable adduct POBN/'H. No detectable yield of hydrated electrons in argon-saturated aqueous solutions at neutral pH was found. These results are evidence against the formation of hydrated electrons as reactive intermediates in the sonochemistry of neutral aqueous solutions.

RESULTS AND DISCUSSION.

The formation of hydrated electrons in neutral aqueous ultrasound-exposed solutions has been postulated previously (1) and arguments were presented in favor and against their existence (see e.g. (2) for a list of related references). The issue of the existence of these species as principal sonochemical intermediates was addressed recently using a sensitive method for detecting the presence of hydrated electrons in argon-saturated water exposed to ultrasound (2).

Nitrone spin traps are particularly suitable for detection of hydrated electrons. The spin trap POBN has been shown to react with e\textsubscript{aq}\textsuperscript{-} with a rate constant of 3.1 x 10\textsuperscript{10} M\textsuperscript{-1} s\textsuperscript{-1} (3):

\[
e\textsubscript{aq}^- + \text{POBN} \rightarrow \text{POBN}^\cdot \rightleftharpoons \text{POBN/'H}
\]

Hence, the EPR detectable adduct of e\textsubscript{aq}\textsuperscript{-} at neutral pH is POBN/'H, identical to the POBN/'H adduct formed by a direct reaction of POBN with \textsuperscript{*}H:

\[
\text{POBN + 'H} \rightarrow \text{POBN/'H}
\]
The formation of hydrated electrons from \(^\bullet\)H atoms in alkaline solutions is well known (4):

\[ \text{H} + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} + \text{e}_{\text{aq}}^- \]

and the pK\(_a\) value of this equilibrium is 9.8. Using the formation of metallic thallium from Tl\(^+\), Gutiérrez et al. (5) have demonstrated the formation of hydrated electrons in the sonolysis of aqueous solutions at pH \(\geq 12.7\). To avoid a significant contribution of this pathway in the formation of hydrated electrons, the current spin trapping experiments were performed at neutral pH.

Cadmium (Cd\(^{2+}\)) is one of the most efficient scavengers of hydrated electrons (6):

\[ \text{Cd}^{2+} + \text{e}_{\text{aq}}^- \rightarrow \text{Cd}^+ \]

and has also been used to study the yield of dry electrons, which are the precursors of e\(_{\text{aq}}^-\) by pulse radiolysis (7). If Cd\(^+\) were formed in our system it would be recycled back to Cd\(^{2+}\) (8):

\[ \text{Cd}^+ + \cdot\text{OH} \rightarrow \text{Cd}^{2+} + \text{OH}^- \]
\[ \text{Cd}^+ + \text{H}_2\text{O}_2 \rightarrow \text{Cd}^{2+} + \cdot\text{OH} + \text{OH}^- \]

or react with another Cd\(^+\) to yield Cd\(^{2+}\) and metallic cadmium (8):

\[ \text{Cd}^+ + \text{Cd}^+ \rightarrow \text{Cd}^{2+} \rightleftharpoons \text{Cd}^0 + \text{Cd}^{2+} \]

At suitably selected concentrations of Cd\(^{2+}\) and POBN, the reaction:

\[ \text{e}_{\text{aq}}^- + \text{POBN} \rightarrow \text{POBN}/\cdot\text{H} \]

can be completely suppressed, while the yield of the reaction of \(^\bullet\)H with POBN will not be changed, because the relative rates of Cd\(^{2+}\) and POBN with e\(_{\text{aq}}^-\) are approximately equal, while POBN reacts \(\geq 10^4\) times faster with \(^\bullet\)H than Cd\(^{2+}\) \((k_{\text{POBN} + \cdot\text{H}} = 3 \times 10^9 \text{ M}^{-1} \text{s}^{-1} \) (9), \(k_{\text{Cd}^{2+} + \cdot\text{aq}}^- = 3.1 \times 10^{10} \text{ M}^{-1} \text{s}^{-1} \) (3), \(k_{\text{Cd}^{2+} + \cdot\text{aq}}^- = 5.4 \times 10^{10} \text{ M}^{-1} \text{s}^{-1} \) (6), \(k_{\text{Cd}^{2+} + \cdot\text{H}} < 3 \times 10^5 \text{ M}^{-1} \text{s}^{-1} \) (6)).

The reaction:

\[ \text{e}_{\text{aq}}^- + \text{H}^+ \rightarrow \cdot\text{H} \ (k = 2.3 \times 10^{10} \text{ M}^{-1} \text{s}^{-1} \) (6))

could not contribute significantly at neutral pH due to the high rates and high concentrations of the competing processes for e\(_{\text{aq}}^-\) removal (reactions of e\(_{\text{aq}}^-\) with POBN and with Cd\(^{2+}\)).

Figure 1 shows the EPR spectra obtained by sonolysis of argon-saturated solutions of H\(_2\)O and D\(_2\)O, containing 2 mM POBN. The comparison of the experimental spectra (Figure 1A and B) with the computer simulated spectra of POBN/\(^\bullet\)H and POBN/\(^\bullet\)D adducts (Figure 1C and D) reveals that the dominant adducts in H\(_2\)O and D\(_2\)O were POBN/\(^\bullet\)H and POBN/\(^\bullet\)D respectively. However, small yields of POBN/\(^\bullet\)H adducts were detected in D\(_2\)O solutions (Figure 1B). This artifactual production of \(^\bullet\)H atoms by pyrolysis of the spin trap has been
Figure 1. EPR spectra of spin adducts produced by 50 kHz sonolysis of neutral argon-saturated H₂O (A), D₂O (B), in the presence of 2 mM POBN. Computer simulations of POBN/^H (C) and POBN/^D (D).

Figure 2. Effect of CdSO₄ (closed symbols) and MgSO₄ (open symbols) concentration on the yield of POBN/^D adducts (A) and on the ferric yield in argon-saturated Fricke dosimeter solution (B) in argon-saturated aqueous solutions exposed to 50 kHz ultrasound.
described previously (10,11) and was the reason for performing all experiments in D₂O, where the measured POBN/D yields originate entirely from the sonolysis of D₂O and can easily be separated from the artifactual POBN/H signal.

The effect of CdSO₄ and MgSO₄ (MgSO₄ was used as a control, since it does not react with \( e_{aq}^- \) or \( {}^*H \) (D) at an appreciable rate, but mimics the potential effect of ionic strength on the reaction rates) on the sonochemical yields of \( {}^*D \) adducts of POBN is shown in Figure 2. If hydrated electrons were formed by sonolysis, a decrease of POBN/D yield with increasing concentration of Cd²⁺ would be expected. However, the yields of POBN/D were unaltered up to approximately 0.1 M Cd²⁺ (Figure 2A) and a similar trend was also observed for Mg²⁺ which served as an ionic strength control (Figure 2B). At 0.1 M Cd²⁺ 98.8% of \( e_{aq}^- \) would be scavenged by Cd²⁺ in the presence of 2 mM POBN. Hence, allowing for a 10% error margin in our measurements, the \( e_{aq}^- \) yield cannot exceed ~10% of the total \( {}^*H \) yield, i.e. less than 0.036 μM \( e_{aq}^-/\text{min} \) would be produced in our system.

Thus, our data show that no detectable yield of hydrated electrons (or less than the detection limit of approximately 0.04 μM/min) is formed in neutral argon-saturated aqueous solutions exposed to 50 kHz ultrasound, thus arguing against the importance of this species as the reactive intermediate in the sonochemistry of neutral aqueous solutions. It would be of interest to ascertain the validity of the present conclusions for the repetitive collapse of a single oscillating sonoluminescent bubble.

REFERENCES.