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Effect of Cd^{2+} on the $^{\bullet}H$ Atom Yield in the Sonolysis of Water. Evidence against the Formation of Hydrated Electrons

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The formation of hydrated electrons in neutral aqueous ultrasound-exposed solutions has been postulated previously, and several arguments were presented in favor and against their existence. 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^{2+} to prevent their reaction with the nitrone spin trap α-(4-pyridyl-1-oxide)-*N*-*tert*-butylnitrone (POBN) to form the EPR-detectable adduct POBN/$^{\bullet}$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.

Introduction

In the 1950s the radiation chemistry of water was explained by the free radicals $^{\bullet}$H and $^{\bullet}$OH and their molecular products H_2 and H_2O_2.[1] The existence of the hydrated electron on theoretical grounds was suggested by Platzman.[2] Experimental studies of the chloroacetate[3] and hydrogen−oxygen−hydrogen peroxide[4] systems provided evidence for a second reducing radical. Final proof of the existence of the hydrated electron was obtained when it was shown that this reducing species possessed unit negative charge[5] and has an intense optical absorption band.[6,7]

The similarities between aqueous sonochemistry and radiation chemistry were explored by a number of investigators starting in the early 1950s.[8−10] Formation of $^{\bullet}$H atoms and $^{\bullet}$OH radicals and their products has been observed in the sonochemistry of aqueous solutions.[11,12] Sonochemistry is due to cavitation, which involves the formation, growth, and collapse of gas microbubbles.[13−15]

Historically, two different theories have been advanced to explain sonochemistry and sonoluminescence (the weak light emitted during cavitation): the thermal ("hot spot")[16] and electrical discharge[17,18] theories. In the thermal theory the adiabatic heating produced by the collapse of cavitation bubbles results in thermal dissociation of water molecules to yield $^{\bullet}$H atoms and $^{\bullet}$OH radicals. The electric discharge theory was proposed by Margulis[18] based on an earlier model of Frenkel.[8] The Margulis theory considers a double layer adjacent to the neck that results from the separation of fragmentation bubbles from a deformed cavitation bubble pulsating in the acoustic field.[18] The physical treatment of the charge separation leading to the electric discharge proposed by Margulis has been criticized recently by Lepoint-Mullie et al.,[19] and the difficulties associated with the electrical discharge hypothesis of sonochemistry were reviewed extensively by Suslick et al.[20]

The electric discharge model suggests the formation of hydrated electrons.[18] Margulis was able to demonstrate chloride formation from chloroacetate;[18,21] this reaction was used in radiation chemistry as evidence for the presence of hydrated electrons. However, during sonolysis chloride ions may be formed from chloroacetate by direct pyrolysis rather than by the reaction with hydrated electrons.[22] Gutiérrez, Henglein, and Dohrmann concluded that hydrated electrons are not formed in the sonolysis of water at neutral pH, based on the absence of colloidal thallium formation in the presence of Tl^+ as e_{aq}^- scavenger ($Tl^+ + e_{aq}^- \rightarrow Tl^0$).[22]

Lepoint and co-workers suggested that the origin of cavitation chemistry could be corona-like discharges caused by a bubble fragmentation process.[23] However, their experimental evidence, based on the existence of a sharp minimum in the $MgCl_2$ concentration-dependent yields of I_3^- produced in the Weissler reaction, could not be reproduced by Gutiérrez et al.[24]

Recently, Margulis concluded that the problem of formation of hydrated electrons as primary products of water decomposition by ultrasound has not been solved, and additional research is needed.[18] New support for the electrical origin ("sparklike process") of sonoluminescence in single oscillating bubbles was presented by Lepoint-Mullie et al.[25] Using the confined electron model of single-bubble sonoluminescence,[26] Bernstein et al. concluded that continuum sonoluminescence can be attributed to transitions of electrons produced by high-temperature ionization and confined to voids in the dense fluid formed during the latter stages of cavitational collapse.[27]

In the current work the possible formation of e_{aq}^- in the sonolysis of neutral aqueous solutions was investigated using Cd^{2+} as an e_{aq}^- scavenger. The formation of e_{aq}^- was evaluated from the decrease in the yield of deuterium adducts of POBN in D_2O. The sensitivity of this method of detection of e_{aq}^- is estimated to be about an order of magnitude greater than the thallium method used by Gutiérrez et al.,[22] in part because of the more favorable ratio of $k_{e_{aq}+Cd^{2+}}/k_{H+Cd^{2+}} > 1.8 \times 10^5$ compared with $k_{e_{aq}+Tl^+}/k_{H+Tl^+} = 4.9 \times 10^2$.[28]

Material and Methods

Chemicals. α-(4-Pyridyl-1-oxide)-*N*-*tert*-butylnitrone (POBN) was acquired from Sigma (St. Louis, MO); deuterium oxide (D_2O, 99.9% atom D) was from Aldrich (Milwaukee, WI). Cadmium sulfate ($3CdSO_4 \cdot 8H_2O$, ACS grade) was obtained from Fisher Scientific Co. (Fairlawn, NJ).

Fricke dosimeter solution was prepared as described: 278 mg of ferrous sulfate ($FeSO_4 \cdot 7H_2O$, Allied Chemical, Morris-

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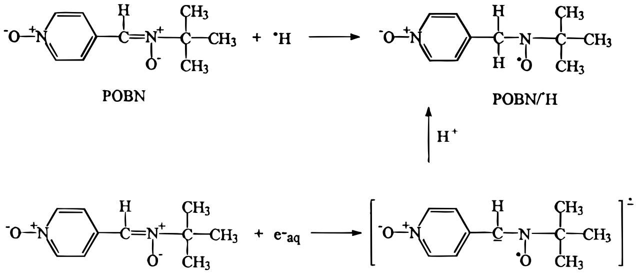

Figure 1. Reactions of POBN spin trap with hydrated electrons and hydrogen atoms.

town, NJ) and 60 mg of sodium chloride were dissolved in 1 L of 0.8 N sulfuric acid. Deuterated Fricke solution was prepared using 0.8 N D_2SO_4 (Aldrich, 98% atom D) in D_2O. To determine the combined sonolytical yields of $^{\bullet}OH$, $^{\bullet}H$, and H_2O_2, Fricke solutions were sonicated under argon, and the optical density at 302 nm (the maximum of Fe^{3+} absorption) was measured. For radiation chemistry in oxygen-free solutions the measured yield of ferric ions is related to the initial yield of reactive intermediates [$G(Fe^{3+}) = 2G_{H_2O_2} + G_{e_{aq}} + G_H + G_{OH} + 3G_{HO_2}$, where G is the number of molecules formed per 100 eV of energy absorbed],[29] and hence the ferric yield is also a useful dosimeter for sonochemistry in aqueous solutions. However, it should be noted that no absolute dosimetry can be defined for sonochemistry because the sonochemical yields not only depend on the total energy deposited in the system but are also critically dependent on the heterogeneous cavitation nuclei in the solution under investigation.

Sonolysis Experiments. An 0.8 mL aliquot of D_2O containing the spin trap POBN was added to a Pyrex test tube, which was fixed in the center of a sonication bath (Bransonic 1200) with a frequency of 50 kHz. The temperature of the coupling water was 20 °C. The sample was sealed with a rubber septum and bubbled with argon through a Teflon tube attached to a fine needle (the argon flow rate was 50 mL/min) for 5 min before sonication and during sonication. After sonication the EPR spectrum of the sample was measured. After each experiment the pH in the samples was measured and was found within a range 6.8 ± 0.2 in all experiments.

EPR Measurements. Immediately after sonication the samples were transferred to EPR quartz flat cells, and the acquisition of the spectrum was started typically within 1 min after the end of sonication. A Varian E-9 X-band spectrometer with 100 kHz modulation frequency and a microwave power of 20 mW was used to record the spectra. The EPR software EPRDAP, written by Dr. Kuppusamy (U.S. EPR, Inc., Clarksville, MD), was used for acquisition, analysis, and simulation of EPR data.

Results and Discussion

Nitrone spin traps are particularly suitable for detection of hydrated electrons. The spin trap POBN has been shown to react with e_{aq}^- with a rate constant of 3.1×10^{10} M^{-1} s^{-1} (Figure 1):[30]

$$e_{aq}^- + \mathrm{POBN} \rightarrow \mathrm{POBN}^{\bullet -} \rightleftharpoons \mathrm{POBN/^{\bullet}H} \qquad (1)$$

Hence, the EPR detectable adduct of e_{aq}^- at neutral pH is POBN/•H, identical to the POBN/•H adduct formed by a direct reaction of POBN with •H (Figure 1):

$$\mathrm{POBN} + {}^{\bullet}\mathrm{H} \rightarrow \mathrm{POBN/^{\bullet}H} \qquad (2)$$

The formation of hydrated electrons from •H atoms in alkaline solutions is well-known:[7]

$$^{\bullet}\mathrm{H} + \mathrm{OH}^- \rightleftharpoons \mathrm{H_2O} + e_{aq}^- \qquad (3)$$

and the pK_a value of this equilibrium is 9.8. Using the formation of metallic thallium from Tl^+, Guttiérrez et al. have demonstrated the formation of hydrated electrons in the sonolysis of aqueous solutions at pH ≥ 12.7.[22] 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:

$$\mathrm{Cd^{2+}} + e_{aq}^- \rightarrow \mathrm{Cd^+} \qquad (4)$$

and has also been used to study the yield of dry electrons, which are the precursors of e_{aq}^-, by pulse radiolysis.[31]

If Cd^+ were formed in our system, it would be recycled back to Cd^{2+}:[32]

$$\mathrm{Cd^+} + {}^{\bullet}\mathrm{OH} \rightarrow \mathrm{Cd^{2+}} + \mathrm{OH^-} \qquad (5)$$

$$\mathrm{Cd^+} + \mathrm{H_2O_2} \rightarrow \mathrm{Cd^{2+}} + {}^{\bullet}\mathrm{OH} + \mathrm{OH^-} \qquad (6)$$

or react with another Cd^+ to yield Cd^{2+} and metallic cadmium: [32]

$$\mathrm{Cd^+} + \mathrm{Cd^+} \rightarrow \mathrm{Cd_2}^{2+} \rightleftharpoons \mathrm{Cd} + \mathrm{Cd^{2+}} \qquad (7)$$

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

$$e_{aq}^- + \mathrm{POBN} \rightarrow \mathrm{POBN/^{\bullet}H} \qquad (8)$$

can be completely suppressed, while the yield of the reaction of •H with POBN will not be changed, because of the relative rates of Cd^{2+} and POBN reactions with e_{aq}^- are approximately equal while POBN reacts $\geq 10^4$ times faster with •H than Cd^{2+} ($k_{\mathrm{POBN+H}} = 3 \times 10^9$ M^{-1} s^{-1},[33] $k_{\mathrm{POBN}+e_{aq^-}} = 3.1 \times 10^{10}$ M^{-1} s^{-1},[30] $k_{\mathrm{Cd^{2+}}+e_{aq^-}} = 5.4 \times 10^{10}$ M^{-1} s^{-1},[28] $k_{\mathrm{Cd^{2+}+H}} < 3 \times 10^5$ M^{-1} s^{-1} [28]). The reaction

$$e_{aq}^- + \mathrm{H^+} \rightarrow {}^{\bullet}\mathrm{H} \quad (k = 2.3 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}})^{28} \qquad (9)$$

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

Figure 2 shows the EPR spectra obtained by sonolysis of argon-saturated solutions of H_2O and D_2O, containing 2 mM POBN. The comparison of the experimental spectra (Figure 2, A and B) with the computer-simulated spectra of POBN/•H and POBN/•D adducts (Figure 2, C and D) reveals that the dominant adducts in H_2O and D_2O were POBN/•H and POBN/•D, respectively. However, small yields of POBN/•H adducts were detected in D_2O solutions (Figure 2B, first peak of the POBN/•H spectrum is labeled with an arrow). This artifactual production of •H atoms by pyrolysis of the spin trap has been described previously[34,35] and was the reason for performing all experiments in D_2O, where the measured POBN/•D yields originate entirely from the sonolysis of D_2O and can be easily separated from the artifactual POBN/•H signal. In addition, small yields of POBN adducts of carbon-centered radicals

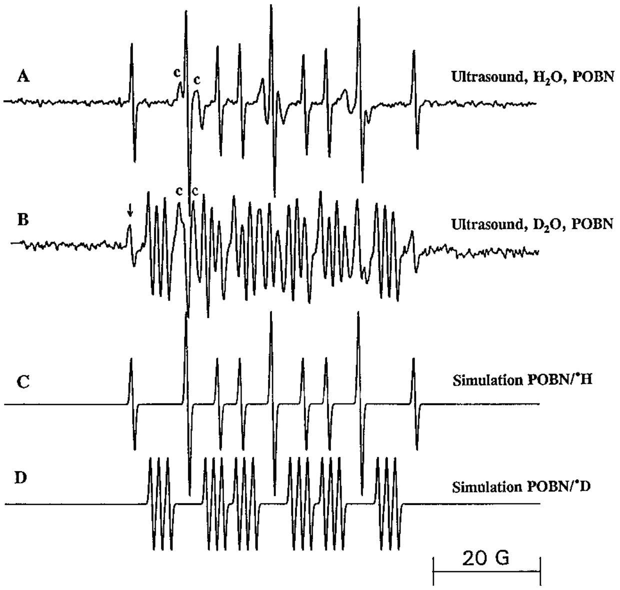

Figure 2. EPR spectra of spin adducts produced by 50 kHz sonolysis of neutral argon-saturated H_2O (A) and D_2O (B) in the presence of 2 mM POBN. Computer simulations of POBN/$^{\bullet}$H (C) and POBN/$^{\bullet}$D (D) adducts obtained using the following splitting constants: $a_N = 16.20$ G, $2a_H = 10.28$ G (POBN/$^{\bullet}$H); $a_N = 16.20$ G, $a_H = 10.28$ G, $a_D = 1.58$ G (POBN/$^{\bullet}$D). The presence of the artifactual POBN/$^{\bullet}$H signal in D_2O is marked by an arrow in spectrum B. (Only the first peak is labeled.) The "c" labels show the positions of the first two peaks of the carbon-centered radical adducts formed by pyrolysis of POBN.

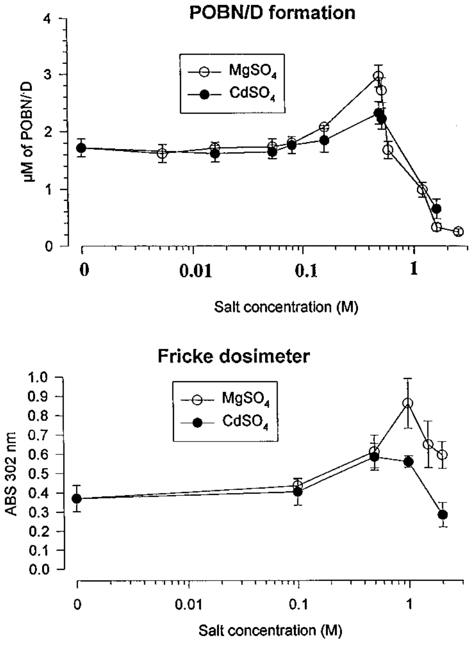

Figure 3. Effect of $CdSO_4$ (closed symbols) and $MgSO_4$ (open symbols) concentration on the yields of POBN/$^{\bullet}$D adducts (A) and on the ferric yield in argon-saturated Fricke dosimeter solution (B) in argon-saturated aqueous solutions exposed to 50 kHz ultrasound.

produced by pyrolysis of the spin trap were detected in both H_2O and D_2O (Figure 2, A and B; first two peaks are labeled "c").[34,35]

The effect of $CdSO_4$ and $MgSO_4$ ($MgSO_4$ was used as a control, since it does not react with e_{aq}^- or $^{\bullet}$H ($^{\bullet}$D) at an appreciable rate but mimics the potential effect of ionic strength on the reaction rates) on the sonochemical yields of $^{\bullet}$D adducts of POBN is shown in Figure 3. If hydrated electrons were formed by sonolysis, a decrease of POBN/$^{\bullet}$D yield with increasing concentration of Cd^{2+} would be expected. However, the yields of POBN/$^{\bullet}$D yields were unaltered up to approximately 0.1 M Cd^{2+} (Figure 3A), and a similar trend was also observed for Mg^{2+} which served as an ionic strength control. At 0.1 M Cd^{2+} 98.8% of e_{aq}^- would be scavenged by Cd^{2+} in the presence of 2 mM POBN. Hence, allowing for a 10% error margin in our measurements, the e_{aq}^- yield would have to be less than ~10% of the total $^{\bullet}$H yield, i.e. less than 0.036 μM e_{aq}^-/min would be produced in our system. Since Cd^{2+} has been shown to be a scavenger of dry electrons, our data also show that no detectable yields of dry electrons were formed by ultrasound. The hypothesis of Bernstein and coworkers[27] of electrons produced by high-temperature ionization and confined to voids in the dense fluid formed during latter stages of cavitational collapse to explain the weak continuum background in sonoluminescence spectra may not be affected by these results, because the emission may be occurring in the gas phase of the bubble, where the charged Cd^{2+} is not likely to be present.

As discussed above, the yields of POBN/$^{\bullet}$D were independent of Cd^{2+} up to 0.1 M of $CdSO_4$, followed by an increase and reaching a maximum at approximately 0.5 M $CdSO_4$, after which the POBN/$^{\bullet}$D yields decreased sharply below the control level (Figure 3A). An identical trend was also observed for $MgSO_4$. The decrease of POBN/$^{\bullet}$D yields at high (above 1 M) concentrations was expected because of the dampening effect of increasing viscosity on cavitation.[24] A similar effect of magnesium chloride on the Weissler reaction was also observed by Gutiérrez et al.[24] However, an unexpected feature that was observed in both $CdSO_4$ and $MgSO_4$ solutions was the increase of POBN/$^{\bullet}$D yields between 0.1 and 0.5 M for both of these solutes (Figure 3A). One possible explanation would be that the observed increase was due to the effect of the ionic strength on the reaction rates of $^{\bullet}$D with POBN. This possibility was excluded by studying the effect of the concentration of these solutes on the yields of the Fricke dosimeter (Figure 3B), which followed the same trend as the POBN/$^{\bullet}$D yields. Although any observed changes at $CdSO_4$ concentrations higher than 0.1 M have no relevance for the discussion of the possibility of the existence of hydrated electrons, they still represent an interesting observation which may be a subject of further studies. The possible effects of these high salt concentrations on the sound velocity, surface tension, water vapor pressure (and hence the effective ratio of the specific heats, γ, in the interior of the bubbles), and the solubility of argon should be considered.

Conclusions

Our data show that no detectable yields of hydrated electrons (or less than the detection limit of approximately 0.04 μM/min) are 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.

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