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pressure range of 1–20 atm. The sonoluminescence intensity was determined to be linearly related to the yield of sonochemical decomposition over the entire range of pressures (1–20 atm).

(5) The sonoluminescence intensity changed by a factor of about 6 over the entire pressure range while the spectral distribution of sonoluminescence was found to be independent of the pressure.

(6) The color temperature of sonoluminescence was estimated to be 4900 ± 600 K over the entire pressure range. This is in agreement with the fact that the spectral distribution of sonoluminescence was independent of pressure.

Registry No. CCl_4, 56-23-5; H_2O, 7732-18-5; HCl, 7647-01-0; HOCl, 7790-92-3.

Chemical Effects of Ultrasound on Aqueous Solutions. Formation of Hydroxyl Radicals and Hydrogen Atoms

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Direct evidence for the formation of ·OH and ·H in the cavitation bubbles produced by ultrasound in argon-saturated aqueous solutions is presented. The methods of spin trapping with 5,5-dimethyl-1-pyrroline 1-oxide (DMPO), 4-[[(1,1-dimethylethyl)imino]methyl]-1-methylpyridinium *N*-oxide (PYBN), and 2-methyl-*N*-(4-pyridinylmethylene)-2-propanamine *N*,*N*′-dioxide (POBN) combined with ESR were used for the detection of ·OH and ·H. With either DMPO or PYBN, the OH and H spin adducts were obtained, and with POBN, the H adduct was observed. These results were confirmed by sonolysis of D_2O solutions containing the same spin traps. By studying the competition reactions for ·OH and ·H between the spin traps, DMPO and POBN, and ·OH and ·H scavengers [O_2, formate, thiocyanate, benzoate, methanol, ethanol, 1-propanol, 2-methyl-2-propanol, acetone, 2-methyl-2-nitrosopropane (MNP)], we obtained further verification for the formation of ·OH and ·H. Sonolysis of aqueous solutions containing DMPO or POBN in the presence of air suppressed formation of H adducts but not that of OH–DMPO. The unusually large effects of acetone and MNP on the spin adduct yields could be explained either by the scavenging of radicals in the gas phase of the cavitation bubbles or by preventing the collapse of the gas bubbles during cavitation and thus reducing radical formation. From the results of the present work, it was inferred that ·OH and ·H are formed in the cavitation bubbles.

Introduction

The study of chemical effects of ultrasound on biological systems[1] is of interest because of the widespread applications of ultrasound in diagnosis and therapy in medicine.[2-4] The collapsing cavities which occur during sonolysis lead to chemical damage and sonoluminescence due to the production of high local instantaneous temperatures and pressures.[5-10] The threshold for cavitation increases with increasing frequency and also depends on factors such as the number of motes (nonwettable particles), nature of the dissolved gases, and the techniques for cavitation detection.[3,11-13]

It has been proposed that ultrasound-induced reactions in aqueous solutions involve free-radical mechanisms due to the formation of hydroxyl radicals (·OH) and hydrogen atoms (·H).[14-23] The effect of volatile scavengers on the formation of hydrogen peroxide during the sonolysis of aqueous solutions was studied by Weissler.[14] It was inferred that H_2O_2 is formed by the recombination of ·OH. However, Anbar and Pecht found that nonvolatile scavengers, in contrast to volatile organic solutes, do not affect the production of H_2O_2 and concluded that H_2O_2 is not formed from ·OH.[17] Weissler also studied ultrasound hydroxylation of benzoic acid which was reported to be due to the formation of ·OH by ultrasound.[15] Anbar and Pecht found that, when deuterated formate anions were sonolyzed in aqueous solutions, HD was produced and the yield of HD was independent of solute concentrations, suggesting that ·H is formed from water by sonolysis.[18] Verrall

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et al.[22] studied the ultrasonic degradation of thymine in aqueous solutions and found that the results could be correlated with those obtained by γ-radiolysis. Wang et al.[23] investigated the decomposition of nucleic bases in aqueous solutions by sonolysis by observing the decrease in solute concentrations as a function of sonication time. However, in spite of a number of suggestions, direct evidence for the formation of the primary radical species was not obtained, and little is known about the mechanism of formation of these species.

Hydroxyl radicals are known to be responsible for the reproductive death of mammalian cells exposed to ionization radiation.[24] The present study reports conclusive evidence for the formation of ·OH and ·H in the cavitation bubbles produced by ultrasound in aqueous solutions. The formation of ·OH and ·H is confirmed by investigating reactions in which ·OH and ·H scavengers [formate, thiocyanate, benzoate, methanol, ethanol, 1-propanol, 2-methyl-2-propanol, acetone, 2-methyl-2-nitrosopropane (MNP)] compete with the spin traps for hydroxyl radicals and hydrogen atoms. Also, by observing the unusually large effects of acetone and MNP in decreasing the formation of spin adducts and the efficient scavenging of ·H by O_2, it was concluded that ·OH and -H are formed in the cavitation bubbles.

Since ·OH and ·H are too short-lived to be observed by conventional ESR, they were spin trapped with nitrone compounds (the spin traps) that convert the short-lived radicals into relatively stable nitroxide radicals (the spin adducts), which are detected by ESR. Recently, it has been reported[25] that short-lived radicals produced by sonolysis of carbon tetrachloride can be spin trapped with MNP and identified by ESR. However, during sonolysis of aqueous solutions containing MNP and a variety of organic solutes (glycylglycine, thymine), no radicals could be spin trapped.[25] In the present work, the nitrone spin traps DMPO, PYBN, and POBN were used since they produce stable OH and H spin adducts.[26-31]

Some preliminary results of this work have been published recently.[32]

Experimental Section

All reagents were purchased from Aldrich and were of reagent grade except PYBN which was obtained from the Spin Trap Co. (Canada). DMPO was purified before use according to the procedure of Buettner and Oberly described previously[33] and the concentrations of aqueous DMPO solutions were determined by UV spectroscopy.[34] POBN and PYBN were used without further purification. Aqueous MNP solutions were prepared by stirring overnight in the dark (1 mg/mL). Bubbling gases into the solution immediately eliminated its pale blue color because of the volatility and the poor solubility of MNP.

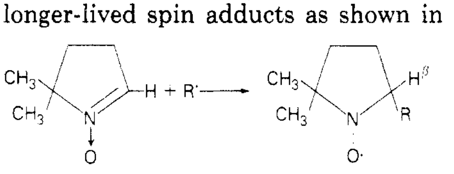
A sample solution (3 mL) was placed in a Pyrex test tube and clamped in the center of a sonication bath (Bransonic 12 ultrasonic bath, frequency and intensity being 50 kHz and of the order of 6×10^2 W/m^2 for air-saturated water, respectively). The sonication time was 3 min while bubbling argon unless otherwise specified. The solutions were Ar-bubbled for 2 min before sonication. When the solutions contained volatile compounds such as acetone and alcohols, argon was bubbled after first passing through another solution with the same concentrations of the volatile component. The level of the liquid inside the sample tube was maintained to be the same as that of the water in the bath, in order to obtain sufficient reproducibility of spin adduct yields.[35] Other experimental conditions were as follows: the temperature of the bath, 23 °C; the flow rate of the bubbled gas, 0.5 L/min.

All samples were sonicated for 3 min which is in the linear region of the plot of the relative ESR intensity (peak-to-peak amplitude) of the spin adduct signals vs. the sonication time (Figure 4, a and b). Concentrations of the spin traps were adjusted so that the ESR signal intensities fall in the plateau region of a plot of the relative ESR intensity of the spin adduct vs. the spin trap concentration (Figure 4, c and d). ESR spectra of sonicated aqueous solutions were measured in an aqueous quartz flat cell (60 mm × 10 mm × 0.25 mm) with a Varian E-9 ESR spectrometer (X-band, 100-kHz field modulation).

Two types of control experiments were carried out. First, the absence of reactions between the spin traps and the scavengers before sonication was verified by monitoring the UV absorbance of the spin traps. Second, the absence of reactions between the scavengers and the H and OH spin adducts was demonstrated by observing the intensity of the ESR spectra. The spin adduct yields were determined by using the stable nitroxide radical (3-carbamoyl-2,2,5,5-tetramethyl-1-pyrroline 1-oxide) as a standard. A calibration curve was determined by plotting the product of the peak-to-peak height of the ESR intensity and the square of the half-height width of the signal vs. different concentrations of the standard nitroxide radical.

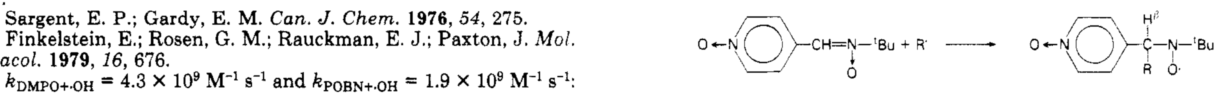
Results and Discussion

The nitrone spin traps used in the present study react with short-lived free radicals generated by sonolysis to produce longer-lived spin adducts as shown in eq 1-3,



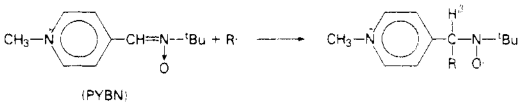
(1)

(DMPO)



(2)

(POBN)



(3)

(PYBN)

where R· is ·OH (or ·OD), ·H (or ·D), or free radicals produced from the scavengers. The spin adducts of these spin traps always have one β-hydrogen except for the H adducts

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TABLE I: Hyperfine Coupling Constants (G) of Spin-Trapped Radicals

spin trap	untrapped radical	a_N	$a_H{}^\beta$	$a_D{}^\beta$	$a_H{}^\gamma$
DMPO	·OH	14.9	14.9		
	·H	16.6	22.5		
	·D	16.6	22.5	3.4	
	$\cdot COO^-$	15.6	18.7		
	$CH_3\dot{C}HOH$	15.8	22.8		
PYBN	·OH	14.7	1.5		0.4
	·H	16.0	10.0		
	·D	16.0	10.0	1.5	
POBN	·H	16.2	10.2		
	·D	16.2	10.2	1.5	
	$\cdot COO^-$	15.5	3.0		
	$CH_3\dot{C}HOH$	15.5	2.6		

which have two hydrogen atoms in β-positions. Therefore, a secondary doublet due to the β-hyrogen is always observed in the ESR spectra while a secondary triplet is obtained in the case of the H adducts.

Evidence for the formation of hydroxyl radicals and hydrogen atoms by sonolysis will be presented next. In Figure 1a, the ESR spectrum obtained from a sonicated aqueous DMPO solution (3.2 mM) is shown. As indicated by the stick diagrams shown in the same figure, this spectrum is due to the OH- and H-DMPO adducts. The hyperfine coupling constants (hfccs), which are listed in Table I, are in good agreement with the values previously reported.[26-29] The ESR spectrum displayed in Figure 1e was obtained from a sonicated D_2O solution containing DMPO (1 mM). Two spectra were found and are assigned to the D-DMPO adduct, as illustrated by the stick diagram, and to the OD-DMPO adduct which is labeled OD in the same figure. The hfccs value of the β-hydrogen of the OD-DMPO adduct is the same as that of the OH-DMPO adduct since further hyperfine lines from the hydrogen in the OH group and the deuterium in the OD group are not usually observed.

By sonicating an aqueous PYBN solution (35 mM), the ESR spectrum shown in Figure 2a was observed. This spectrum is composed of three components, namely, a 3 × 3, a 3 × 2 × 2, and a 3 × 2 (broad, not assigned) sets of lines. In order to assign these spectra, UV photolysis in the presence of H_2O_2 and γ-radiolysis of aqueous PYBN solutions were studied. The ESR spectrum displayed in Figure 2b was obtained by UV photolysis (at λ = 265 nm) of aqueous PYBN solutions (25 mM) containing H_2O_2 (5 λ of 30% H_2O_2 per 1 mL). This experiment was carried out in situ in an aqueous ESR quartz cell with a Hg-Xe lamp combined with a grating monochromator (Shoeffel 1000-W). The stick diagram in Figure 2b shows the 3 × 2 × 2 lines with equal intensity due to the nitroxide nitrogen, a β-hydrogen, and the γ-hydrogen of the OH group. The hfccs obtained in the present work are in agreement with the values reported previously.[30] Consquently, one of the spectra in Figure 2a that consists of 3 × 2 × 2 lines is assigned to the OH-PYBN adduct. This spectrum was not always observed in the sonolysis study of aqueous PYBN solutions because of the short lifetime of the OH adduct. Also, γ-radiolysis (dose, 300 krd) of aqueous PYBN solutions (25 mM) gave rise to the ESR spectrum shown in Figure 2c which consists of a major component, 3 × 3 lines, and a minor one, 3 × 2 lines (broad), see Table I. The major component is assigned to the H-PYBN adduct since the only spin adduct of PYBN that has two equivalent β-hydrogen atoms is the H-PYBN adduct. Hydrogen atoms are known to be generated by γ-radiolysis of water. However, the present assignment is not con-

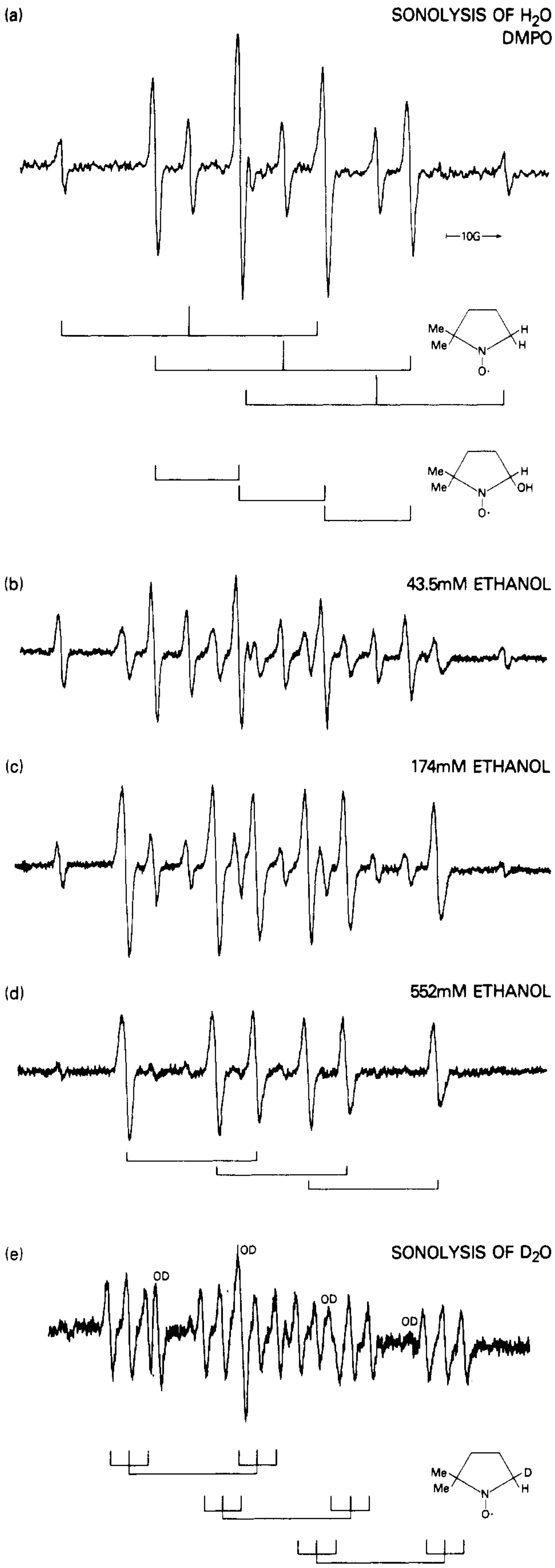

Figure 1. ESR spectra of spin-trapped radicals obtained by sonolysis (3 min) from aqueous solutions containing DMPO (75 mM) and ethanol ((a) none; (b) 43.5 mM; (c) 174 mM; (d) 552 mM); (e) a D_2O solution containing DMPO (1 mM). Spectrometer settings are as follows: modulation amplitude, 0.63 G; receiver gain, 4.0 × 10^4 for (a), 6.3 × 10^4 for (b), (c), and (d) and 2.0 × 10^5 for (e); time constant, 0.5 s for (a), (b), (c), and (d) and 1 s for (e); scan time, 8 min for (a), 30 min for (b), (c), and (d), and 1 h for (e).

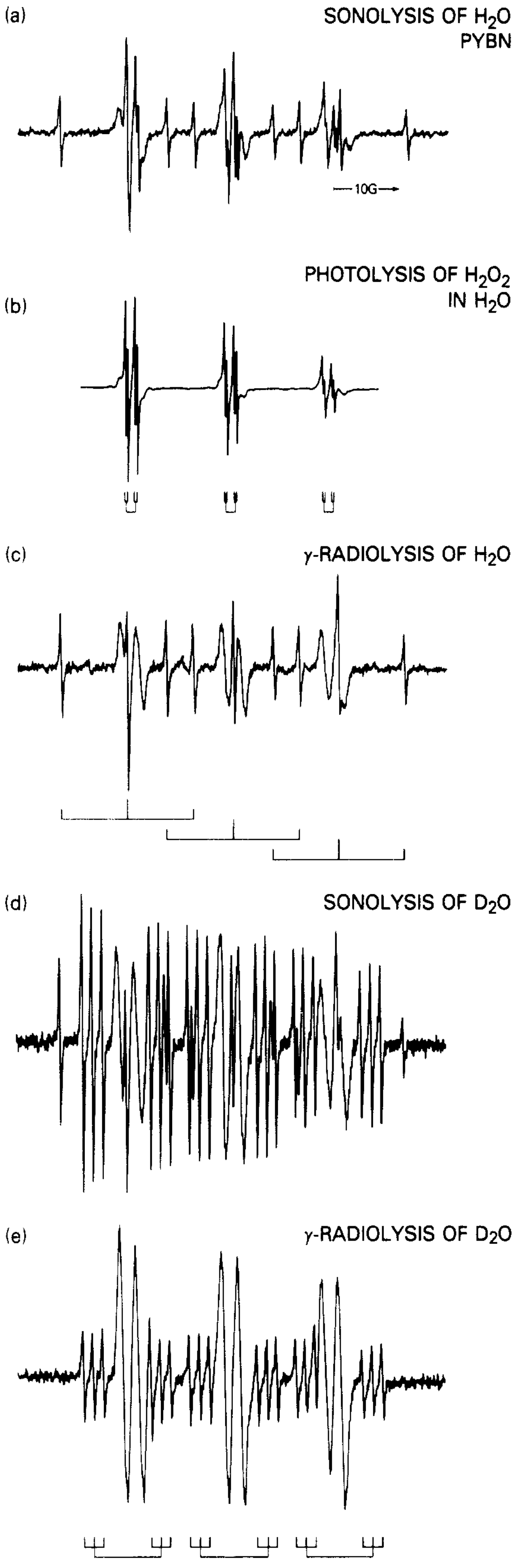

Figure 2. ESR spectra of spin-trapped radicals obtained from (a) an aqueous PYBN (25 mM) solution by sonolysis (3 min); (b) an aqueous PYBN (25 mM) solution containing H_2O_2 (40 mM) photolyzed at 265 nm; (c) an aqueous PYBN (25 mM) solution by γ-radiolysis (total dose, 300 krd); (d) a D_2O solution containing PYBN (25 mM) by sonolysis (3 min); (e) a D_2O solution containing PYBN (25 mM) by γ-radiolysis (total dose 300 krd). Spectrometer settings are as follows: modulation amplitude, 0.2 G for (a), (c), (d), and (e), 0.1 G for (b); receiver gain, 2.5×10^3 for (a) and (c), 1.25×10^3 for (b), and 1.25×10^5 for (d) and (e); time constant, 0.128 s for (a), 0.032 s for (b), 0.25 s for (c), 0.5 s for (d), and 1 s for (e); scan time, 8 min for (a), 16 min for (b) and (c), 30 min for (d), and 1 h for (e).

sistent with that reported previously.[30] In order to confirm our assignment, D_2O solutions containing PYBN (25 mM) were sonicated or γ-irradiated. The resulting spectra are shown in Figure 2, d and e, respectively. In Figure 2e, the observed 3 × 2 lines due to the nitroxide nitrogen and a β-hydrogen further split into 3 lines due to a β-deuterium are shown. The hfccs, a_N and $a_H{}^\beta$, are in good agreement with those of the H-PYBN adduct in Figure 2c. The observed $a_D{}^\beta$ is consistent with the expected value $a_H{}^\beta/6.52$, the ratio of the gyromagnetic ratios of H and D. Hence this radical is attributed to the D-PYBN adduct. Sonolysis of a D_2O solution of PYBN led to the ESR spectrum displayed in Figure 2d, where the same 3 × 2 × 3 lines as those shown in Figure 2e (D-PYBN) and the unexpected 3 × 3 lines of H-PYBN were observed. A tentative explanation for the formation of the H-PYBN adduct in a (% D > 99%) D_2O solution could be due to an ultrasound-induced H-D exchange reaction between the D-PYBN adducts and PYBN molecules.

Further evidence for the formation of hydrogen atoms was obtained with POBN. Figure 3a shows the ESR spectrum obtained by sonolysis of an aqueous POBN solution (25 mM). It has been reported[31] that the lifetime of the OH-POBN adduct is too short to be observable by conventional ESR (being of the order of seconds) except by in situ UV photolysis. As illustrated by the stick diagram (Figure 3a), the formation of the H-POBN adduct was observed. Sonolysis of a D_2O solution of POBN resulted in an ESR spectrum (Figure 5e) which has 3 × 2 × 3 lines of equal intensity due to the nitroxide nitrogen, a β-hydrogen, and a β-deuterium. In this case, the ESR spectrum due to the H-POBN adduct was also found. All hfccs are listed in Table I and they are consistent with the values reported previously.[36]

The effects of increasing the sonolysis time on the ESR signal intensity were studied as a function of the nature of the bubbled gases. The resulting data obtained for the OH-DMPO adduct and the H-POBN adduct are presented in Figure 4, a and b, respectively. When argon or nitrogen gas was bubbled through the solutions before and during sonolysis, the ESR signal intensity of the OH-DMPO and the H-POBN adducts increased with the time of sonolysis and reached a plateau above about 15- and 25-min sonolysis, respectively. The ESR signal intensity of these adducts was found to be larger with Ar than with N_2. Dissolved gases of low thermal conductivity (e.g., Ar) produce greater sonochemical yields than those of high conductivity.[37] On the other hand, during air bubbling, the intensity of the OH-DMPO spin adduct increased linearly as a function of the sonolysis time.

When aqueous DMPO solutions (3.2 mM) were sonicated during air bubbling or in the presence of air, only the ESR spectrum due to the OH-DMPO adduct, but not that of the H-DMPO adduct, was observed. Sonolysis of air-saturated aqueous solutions containing POBN (25 mM) led to the spectrum which only consists of 3 × 2 lines. However, from an aqueous solution of POBN sonicated with Ar bubbling, 3 × 3 lines due to the H-POBN adduct (Figure 3a) were obtained. These results are consistent with O_2 scavenging ·H in the cavitation bubbles. This explanation is supported by γ-radiolysis experiments. When aqueous DMPO (3.2 mM) or POBN (25 mM) solutions were γ-irradiated in the presence of air to a dose of 100 krd, the H-spin adducts were observed. If hydrogen atoms were formed by ultrasound in the bulk of the so-

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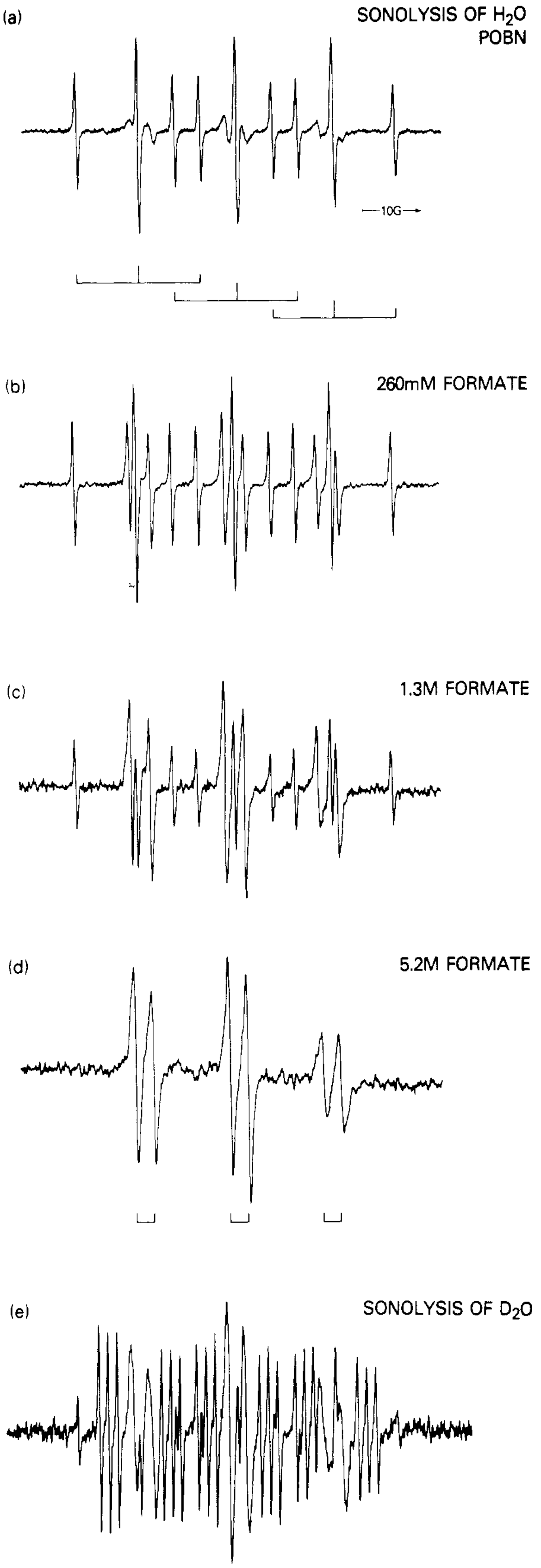


Figure 3. ESR spectra of spin-trapped radicals obtained by sonolysis (3 min) from (a), (b), (c), and (d), an aqueous solution containing POBN (25 mM) and sodium formate ((a) none, (b) 260 mM, (c) 1.3 M, and (d) 5.2 M); (e) a D_2O solution containing POBN (25 mM). Spectrometer settings are as follows: modulation amplitude, 0.4 G; receiver gain, 2.0×10^3 for (a), 3.2×10^4 for (b), 6.3×10^4 for (c), 2.5×10^5 for (d), and 1.25×10^5 for (e); time constant, 0.25 s for (a), (b), and (c), 2.0 s for (d) and (e); scan time, 8 min for (a), (b), and (c), 30 min for (d), and 1 h for (e).

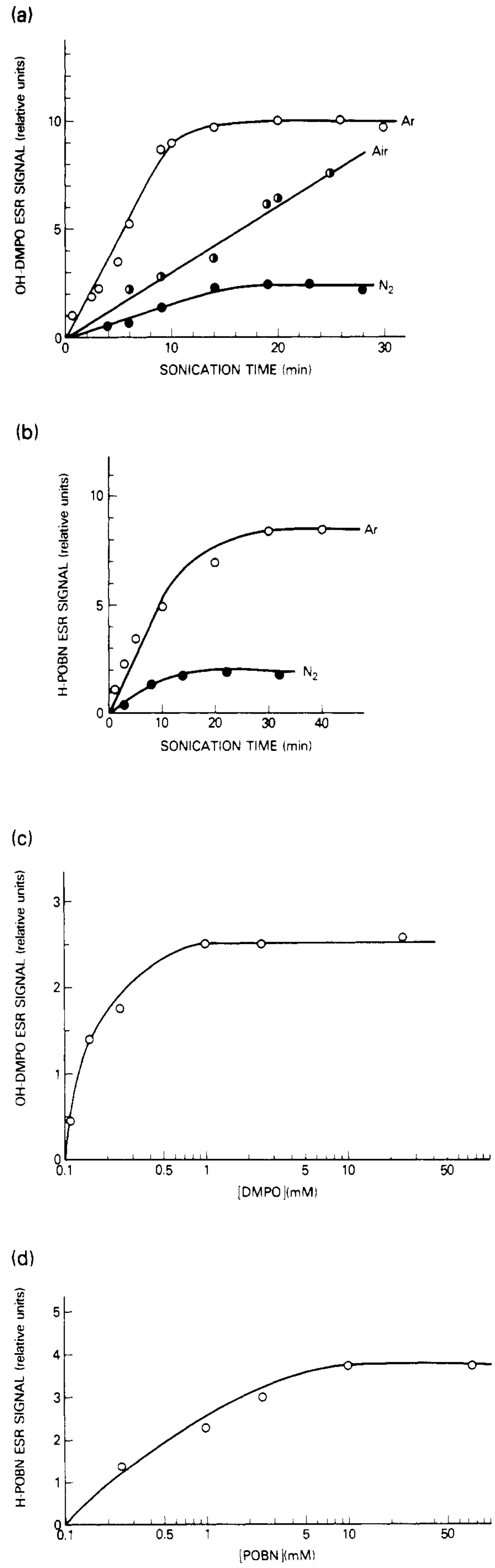


Figure 4. Sonication time dependence of ESR intensity of (a) the OH–DMPO adduct and (b) the H–POBN adduct. Concentrations of the spin traps are as follows: 3.2 mM DMPO and 25 mM POBN. Spin trap concentration dependence of ESR intensity of (c) the OH–DMPO adduct and (d) the H–POBN adduct. Sonication time is 3 min.

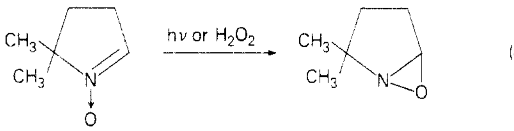
lution, dissolved O_2 (0.2 mM) could not compete with the spin traps for ·H.[38,39] This result can be predicted from the known values of the rate constants of the reactions of O_2 and the spin traps (DMPO and POBN) with ·H. Hence it can be concluded that ·H is formed in the cavitation bubbles by ultrasound in aqueous solutions.

The effect of the spin trap concentration on the OH–DMPO and H–POBN spin adduct yields was investigated. As shown in Figure 4, c and d, when aqueous solutions containing either DMPO or POBN were sonicated during Ar bubbling, the ESR intensities of the OH–DMPO and the H–POBN spin adducts increased with the spin trap concentration and reached a plateau at about 1 and 10 mM, respectively. This result is consistent with spin adduct formation by a free-radical mechanism.

The spin adduct yields were determined by using the stable nitroxide radical, 3-carbamoyl-2,2,5,5-tetramethylpyrroline 1-oxide as a standard. With DMPO and POBN concentrations of 3.2 and 25 mM, respectively, the spin adduct concentrations were as follows: OH-DMPO adduct, 0.18 μM at 3 min and 0.67 μM in the plateau region of Figure 4a; H-POBN adduct, 0.05 μM at 3 min and 0.22 μM in the plateau region of Figure 4b. On the basis of these results, the 3-min sonication time used in the present work was chosen since the radical yield is a linear function of sonication time at this value.

The results obtained by sonolyses of aqueous solutions containing either DMPO, PYBN, or POBN are consistent with the formation of ·OH and ·H by ultrasound in aqueous solutions. Also, the observation of the ESR spectra due to the D adducts of these three spin traps confirms the formation of hydrogen atoms from water. Furthermore, the unusual scavenging effect of O_2 indicates that these primary species are produced in the cavitation bubbles generated by ultrasound in aqueous solutions.

It has been reported that there are three other reaction pathways that produce the OH and H adducts which do not involve the formation of ·OH and ·H. First, DMPO can be converted into the isomeric oxazirane by photochemical rearrangement or by reaction with H_2O_2[40] as shown in eq 4. The hydrolysis of the epoxy ring shown in eq 5 leads to the production of the hydroxylamine, which is oxidized to form the same nitroxide radical as obtained by spin trapping of ·OH with DMPO. Second, the hydroxyl adduct of POBN can be produced by acid-catalyzed addition of water followed by H_2O_2 addition.[31] Since the formation of H_2O_2 from water can occur by sonolysis, it is conceivable that the OH–PYBN adduct could be similarly produced. Third, the hydrogen adducts could be produced by the reaction of hydrated electrons (e_{aq}^-) with all three spin traps followed by protonation.



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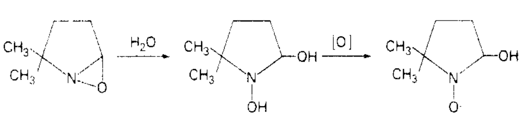

(5)

Direct formation of ·OH and ·H from water by sonolysis rather than these other pathways was verified by carrying out experiments in which scavengers compete with the spin traps, DMPO and POBN, for ·OH and ·H. The literature values of the rate constants for the reactions between the spin traps and the scavengers used in this study with ·OH and ·H as well as e_{aq}^- are known.[38,39,41–43] First, the effect of scavengers on the formation of ·OH was investigated. When aqueous DMPO solutions containing various concentrations of sodium formate were sonicated, a decrease in the signal of the OH–DMPO adduct and a corresponding increase of the CO_2^-–DMPO adduct[28,44] was observed as the formate concentration was increased at constant DMPO concentration.[32] The CO_2^-–DMPO adduct is formed as follows:

$$HCOO^- + \cdot OH \rightarrow \cdot COO^- + H_2O \qquad (6)$$

$$\cdot COO^- + DMPO \rightarrow CO_2^-\text{–}DMPO \qquad (7)$$

These changes indicate that competitive scavengings of ·OH by DMPO and $HCOO^-$ has occurred since the change in the ESR spectra occurs when the product of the reaction rate (k) and the concentration (c), $k_{HCOO^-+\cdot OH}[HCOO^-]$, is comparable to $k_{DMPO+\cdot OH}[DMPO]$. Analogous experiments with DMPO and ethanol were performed by changing the ethanol concentration at constant DMPO concentration (75 mM). As a function of ethanol concentration, the ESR intensity of the OH–DMPO adduct decreased whereas that of the $CH_3CH(OH)$–DMPO adduct[28,45] increased, as shown in Figure 1a–d. The $CH_3CH(OH)$–DMPO adduct (Figure 1d) is produced by H abstraction followed by addition to DMPO, as shown in eq 8 and 9.

$$CH_3CH_2OH + \cdot OH \rightarrow CH_3\dot{C}HOH + H_2O \qquad (8)$$

$$CH_3\dot{C}HOH + DMPO \rightarrow CH_3CH(OH)\text{–}DMPO \qquad (9)$$

Figure 5a summarizes the effects of various scavengers on the OH–DMPO yield produced by sonolysis of Ar-bubbled and air-saturated solutions. The relative intensity of the OH–DMPO ESR signal is shown as a function of $k_{scavenger+\cdot OH}$[scavenger]. In Ar-bubbled solutions the scavengers used were formate, thiocyanate, methanol, 2-methyl-2-propanol, and acetone while in air-saturated solutions formate, ethanol, acetone, and 2-methyl-2-nitrosopropane (MNP) were studied. The ESR intensity of the OH–DMPO adduct decreases as a function of kc. For radical competition reaction in homogeneous solutions, the data for all scavengers would be expected to fit a single curve in Figure 5a. Small deviations of behavior between the scavengers (formate, thiocyanate, methanol, ethanol, and 2-methyl-2-propanol) can perhaps be understood in terms of ·OH and the scavengers reacting not only in the bulk of the solution but also at the interface between the aqueous solution and the gaseous phase. In addition, the effect of the other ·OH scavengers, bromide, bicarbonate, and benzoate, on the yield of the OH–DMPO adduct was

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(38) $k_{scavenger+\cdot H}$ ($M^{-1}\ s^{-1}$): 3×10^8 ($HCOO^-$), 2.7×10^8 (CNS^-), 1.4×10^9 ($C_6H_5COO^-$), $<5 \times 10^4$ (Cd^{2+}), 3.4×10^4 (HCO_3^-), 4.7×10^6 (methanol), 3×10^7 (ethanol), 4×10^7 (1-propanol), 6.4×10^5 (acetone), and 2×10^{10} (O_2): Anbar, M.; Farhataziz; Ross, A. B. *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand. No. 51.*

(39) $k_{POBN+\cdot H} = 3 \times 10^9\ M^{-1}\ s^{-1}$: Greenstock, C. L., private communication.

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(41) $k_{scavenger+\cdot OH}$ ($M^{-1}\ s^{-1}$): 3×10^9 ($HCOO^-$), 7.5×10^9 (CNS^-), 6×10^9 ($C_6H_5COO^-$), $<10^5$ (Cd^{2+}), 1×10^9 (Br^-), 1.5×10^7 (HCO_3^-), 9×10^8 (methanol), 1×10^9 (ethanol), 2.6×10^9 (1-propanol), 4×10^9 (2-methyl-2-propanol), and 9×10^7 (acetone): Farhataziz; Ross, A. B. *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand. No. 59.*

(42) $k_{scavenger+e_{aq}^-}$ ($M^{-1}\ s^{-1}$): $<10^4$ ($HCOO^-$), $<10^6$ (CNS^-), 3.1×10^9 ($C_6H_5COO^-$), 5×10^{10} (Cd^{2+}), $<10^6$ (HCO_3^-), $<10^5$ (ethanol), and 6×10^9 (acetone): Bambenek, M.; Ross, A. B. *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand. No. 43.*

(43) $k_{MNP+\cdot OH} = 5 \times 10^9\ M^{-1}\ s^{-1}$ and $k_{MNP+\cdot H} = 1 \times 10^9\ M^{-1}\ s^{-1}$: Greenstock, C. L. *Abstr. Meeting Chem. Inst. Can. 61st.* **1978**, *5*.

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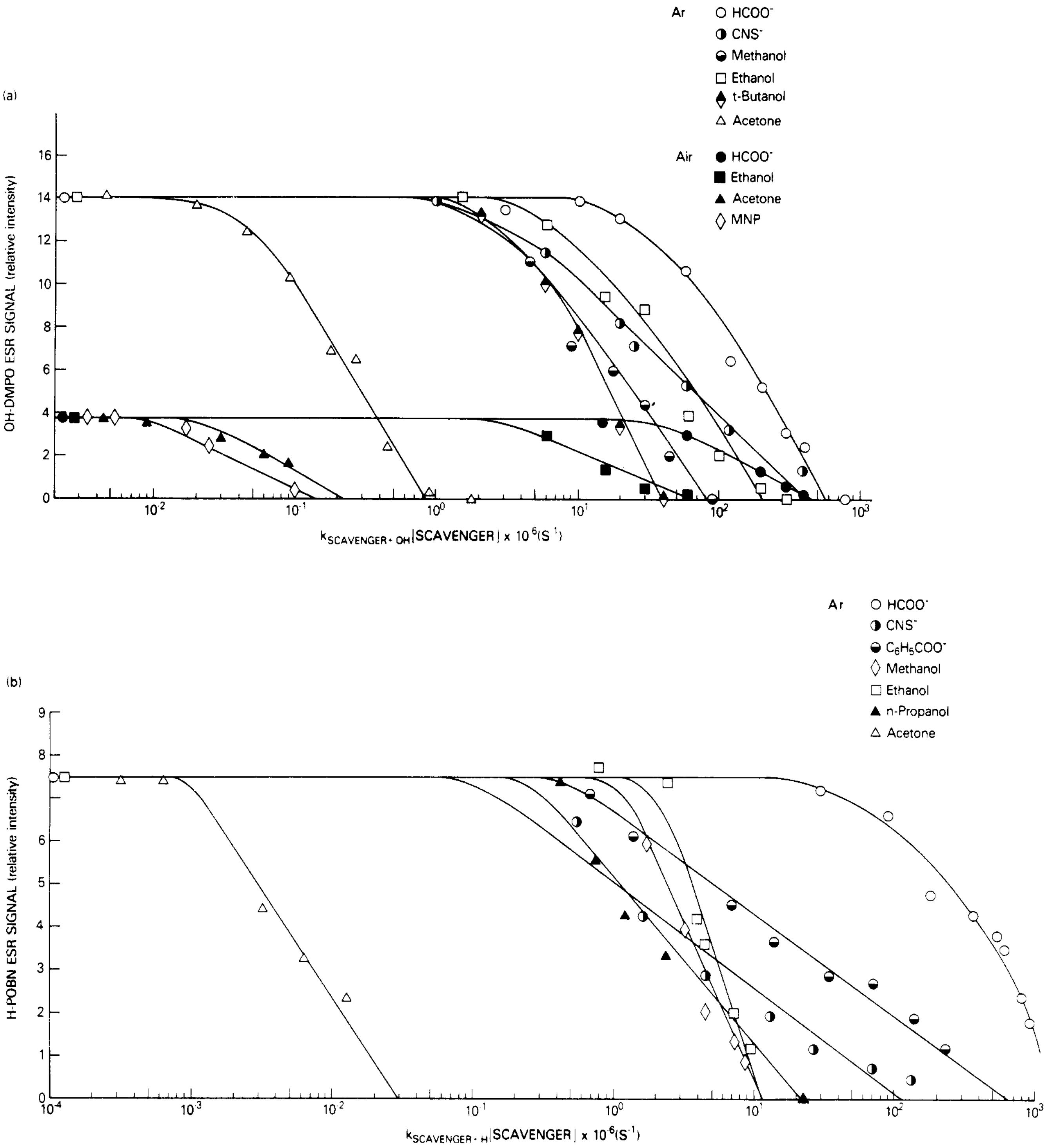

Figure 5. Effects of various scavengers on the formation of the spin adducts ((a) OH-DMPO, (b) H-POBN). The change in the ESR intensities of the spin adducts is plotted vs. the products of the rate constants of the scavengers and the concentrations of the scavengers.

studied. Known quantities of these scavengers were added to aqueous DMPO solutions so that after sonolysis a 50% decrease in the ESR intensity of the OH-DMPO adduct can be observed relative to that obtained in the absence of the scavenger. Since $k_{\mathrm{HCO_3^-+\cdot OH}}$ is 100 times smaller than those of bromide and benzoate,[41] a 100 times higher concentration of bicarbonate was needed in order to obtain a 50% reduction in the OH adduct ESR signals.

The results obtained by studying the competition reactions for ·OH between DMPO and various scavengers strongly indicate that ·OH is formed by ultrasound from water. In addition to this, as shown in Figure 5a, acetone and MNP react with ·OH as if their rate constants were two orders of magnitude greater than the known values for acetone[41] and MNP[43] in homogeneous solutions. The effective monomer MNP concentration was calculated from the monomer–dimer ratio for aqueous MNP solutions at room temperature which is about 0.5.[46] Compared to the effect of the other scavengers, the unusual behavior of acetone and MNP indicates that ·OH is produced in the cavitation bubbles generated by ultrasound in aqueous solutions. It has been reported[25] that MNP could not spin trap free radicals produced by ultrasound in aqueous solutions containing organic solutes, except the *tert*-butyl radical. The results obtained in the present study suggest

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the possibility that MNP reacts with ·OH in the cavitation bubbles so that hydroxyl radicals cannot diffuse into the bulk of solution to react with the solutes. Since the OH and H spin adducts of MNP are known to be unstable,[47] no ESR spectrum except that of the di-*tert*-butyl nitroxide radical which is produced by the reaction of MNP with the *tert*-butyl radical generated from MNP[48] by ultrasound can be observed. This could explain why the previous attempts to spin trap free radicals produced by ultrasound in aqueous solutions containing organic solutes (e.g., glyclglycine, thymine) and MNP were unsuccessful.[25] Alternatively, MNP and acetone by virtue of their high vapor pressure might prevent effective collapse of the gas vacuoles during cavitation and thus reduce the yield of hydroxyl radicals.

In order to study the effect of scavengers on the formation of ·H, we performed analogous experiments with POBN during Ar bubbling. The scavengers used were formate, thiocyanate, benzoate, methanol, ethanol, 1-propanol, and acetone. In Figure 3, a–d, the decrease in the ESR intensity of the H–POBN adduct and the increase of the CO_2^-–POBN adduct are displayed as a function of the formate concentration at constant POBN concentration (25 mM). Also, as shown in Figure 6, with ethanol, the H–POBN adduct intensity decreased as the ethanol concentration was raised whereas the $CH_3CH(OH)$–POBN adduct[28] intensity increased. The stick diagram for the $CH_3CH(OH)$–POBN adduct is shown in Figure 6d. Since ethanol does not react with e_{aq}^-,[42] this result suggests the direct formation of ·H from water by ultrasound. When the pH of Ar-bubbled POBN solution was varied from 5 to 10, the ESR intensity of the H–POBN adduct produced by sonolysis solutions did not change. Since there is an equilibrium between ·H and e_{aq}^- ($H_2O + e_{aq}^- \rightleftarrows$ ·H + OH^-), these results suggest that the H–POBN adduct is formed only from ·H. Further support for this conclusion was obtained by sonolysis of aqueous POBN solutions (25 mM) containing Cd^{2+} (300 μM), a well-known e_{aq}^- scavenger,[42] since no decrease in the ESR intensity of the H–POBN adduct was observed. Consequently, it is inferred that hydrogen atoms are formed from water by ultrasound.

In order to verify the formation of ·H in the cavitation bubbles produced by sonolysis of water, as suggested in the study of the effect of dissolved O_2 on the formation of the H–POBN adduct by ultrasound, we performed further scavenging experiments. As shown in Figure 5b, the ESR intensity of the H–POBN adduct is plotted against the product of the rate constants ($k_{\text{scavenger+·OH}}$) and the concentrations of the scavengers. When the concentrations of the scavengers were increased at constant POBN concentration (10 mM), a decrease in the ESR signals of the H–POBN adduct was produced. This indicates competition reactions for ·H between POBN and the scavengers. The deviation among the plots for the scavengers (formate, thiocyanate, benzoate, methanol, ethanol, and 1-propanol) may be explained by the same arguments suggested for the OH–DMPO adduct (Figure 5a). Acetone reacted with ·H as if its rate constant were three orders of magnitude greater than the known value obtained from studies of homogeneous aqueous solutions,[38] indicating either that acetone reacts with ·H in the cavitation bubbles or prevents the formation of hydrogen atoms by interfering with the cavitational process. Consequently, it is inferred that hydrogen atoms, like hydroxyl

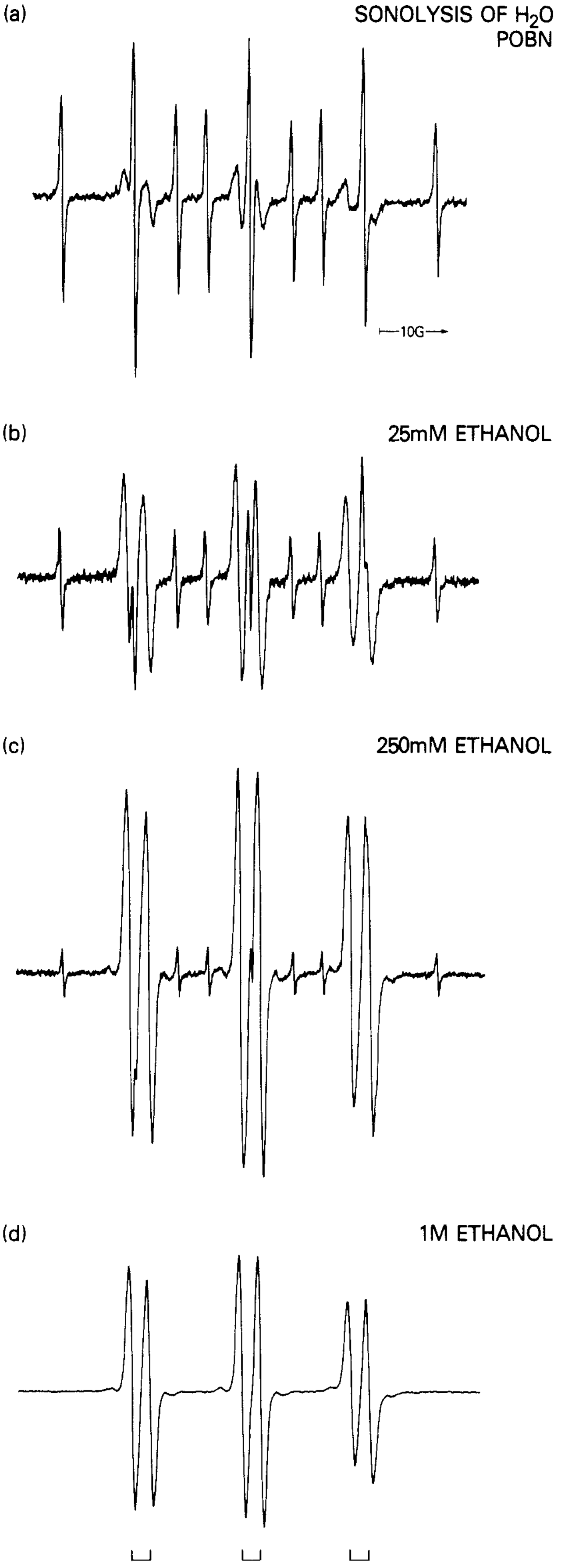

Figure 6. ESR spectra of spin-trapped radicals obtained by sonolysis (3 min) from an aqueous solution containing POBN (25 mM) and ethanol ((a) none; (b) 25 mM; (c) 250 mM; (d) 1 M). Spectrometer settings are as follows: modulation amplitude; 0.4 G; receiver gain, 4.0 × 10^4 for na), 5.0 × 10^4 for (b), 2.5 × 10^4 for (c), and 1.25 × 10^4 for (d); time constant, 0.25 s; scan time, 16 min.

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radicals, are formed in the cavitation bubbles produced by ultrasound in aqueous solutions.

Summary

Hydroxyl radicals and hydrogen atoms are produced by ultrasound in aqueous solutions. ·OH and ·H formed by ultrasound in aqueous solutions were spin trapped with DMPO and PYBN while with POBN the H–POBN adduct was obtained. Furthermore, sonolysis of D_2O solutions containing the same spin traps led to the formation of the D spin adduct. This is in good agreement with the previous work of Anbar and Pecht.[18] These results were confirmed by investigating the competition reactions for ·OH and ·H between the spin traps (DMPO and POBN) and the ·OH and ·H scavengers (O_2, formate, thiocyanate, benzoate, Br^-, bicarbonate, methanol, ethanol, 1-propanol, 2-methyl-2-propanol, acetone, and MNP). The unusual effects of O_2, acetone, and MNP indicate that ·OH and ·H are produced in the cavitation bubbles and not in the bulk of the solution.

Registry No. DMPO, 3317-61-1; PYBN, 69396-86-7; POBN, 66893-81-0; MNP, 917-95-3; HO·, 3352-57-6; H·, 12385-13-6; O_2, 7782-44-7; D_2O, 7789-20-0; H_2O, 7732-18-5; ·COO^-, 14485-07-5; $CH_3(OH)CH$·, 2348-46-1; D·, 16873-17-9; OH–DMPO adduct, 55482-03-6; H–DMPO adduct, 40936-29-6; D–DMPO adduct, 80402-70-6; CO_2^-–DMPO adduct, 84895-13-6; $CH_3CH(OH)$–DMPO adduct, 40936-18-3; OH–PYBN adduct, 69397-28-0; H–PYBN adduct, 69397-35-9; D–PYBN adduct, 84895-14-7; H–POBN adduct, 81616-73-1; D–POBN adduct, 84895-15-8; CO_2^-–POBN adduct, 84895-16-9; $CH_3CH(OH)$–POBN adduct, 84895-17-0; formate, 71-47-6; thiocyanate, 302-04-5; benzoate, 766-76-7; methanol, 67-56-1; ethanol, 64-17-5; 1-propanol, 71-23-8; 2-methyl-2-propanol, 75-65-0; acetone, 67-64-1.

Structure of Micellar Solutions of Nonionic Surfactants. Nuclear Magnetic Resonance Self-Diffusion and Proton Relaxation Studies of Poly(ethylene oxide) Alkyl Ethers

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Binary systems of water and nonionic surfactants of the dodecyl oxyethylene monoether type, $C_{12}H_{25}$-$(OCH_2CH_2)_nOH$, have been studied by ^1H NMR techniques. For $n = 5$, $C_{12}E_5$, and $n = 8$, $C_{12}E_8$, the self-diffusion coefficients of the surfactants in the isotropic, L_1, phase have been measured by using the pulsed field gradient technique for a range of temperatures and concentrations. In addition, the line widths of the different proton signals have been monitored, and some samples of liquid crystalline character were also studied. Dramatic broadening of the methylene signals of the C_{12} chain is observed as the hexagonal liquid crystalline phase is approached in the $C_{12}E_5$–water system, while only a small broadening is observed in the $C_{12}E_8$–water system, showing that at low temperatures there is a growth of $C_{12}E_5$ micelles to rods with increasing concentrations, while the $C_{12}E_8$ micelles at low temperatures remain small in the whole concentration range. The self-diffusion coefficients of the surfactants decrease rapidly with increasing concentration until a minimum is reached after which there is a slow increase. The location of the minimum occurs at lower surfactant concentrations the closer the temperature is to the cloud point, where the system separates into two isotropic phases. In the line width studies, broadening is found at a certain temperature interval when the temperature is increased in the $C_{12}E_5$ system. These results taken together indicate that, in the $C_{12}E_5$ system, the surfactant aggregates grow in size as the cloud point is approached. The aggregates seem to be flexible and probably not of a definite shape close to the cloud point. In the $C_{12}E_8$ system, the micelles are much less affected by an increase in temperature and micellar growth cannot be unambiguously established. The methylene signals of the ethylene oxide moieties consistently show narrower ^1H signals, showing that in the aggregates they are less ordered than the chain methylenes. The various changes in aggregate size and shape are correlated with the stability ranges of the isotropic and liquid crystalline phases according to phase diagrams from the literature. Both aggregate size and phase structures are in qualitative agreement with considerations based on the effective (as a result of coiling, hydration, and head group size) shape of the molecules at different temperatures and concentrations.

Introduction

With increasing temperature, dilute solutions of nonionic surfactants of the ethylene oxide variety split into two water-rich isotropic phases. This occurs throughout a region of coexistence, from above the lower to below the upper critical temperature. The phenomenon has been attributed to a dehydration of the surfactant head groups with increasing temperature.[2-5] The changes in aggregate structure accompanying this phase separation are still not well understood. Results from several experimental methods—light scattering,[6,7] membrane osmometry,[8] sedimentation equilibrium,[9] and viscosity[7,9]—can be inter-

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