H Atom Reactions in the Sonolysis of Aqueous Solutions

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Aqueous solutions of the spin trap 5,5-dimethylpyrroline N-oxide (DMPO) and of Br₂, I₂, MnO₄⁻, AuCl₄⁻, and Ag⁺ were irradiated with 1-MHz ultrasound under argon-hydrogen mixtures of various compositions. DMPO was found to trap only very small amounts of hydrogen atoms while substantially greater amounts could be scavenged by the other solutes. The yield of H atoms as measured by the ESR signal of the DMPO adduct decreased with increasing H_2 concentration in the gas mixture. The yields of the reduction products of the other solutes passed through a maximum at about 20 vol % H₂. The efficiency of scavenging did not correlate to the rate constant of reaction with H in homogeneous solution. It seems that the ability of a solute to be accumulated at the liquid-gas interface of cavitation bubbles strongly influences the scavenging efficiency. Thallium ions are reduced in solutions of high pH. This reduction is attributed to hydrated electrons which are formed in the reaction of the H atoms with OH- anions. It is concluded that the local concentration of H atoms in the interfacial region of the cavitation spots is about 10^{-3} M and that hydrated electrons are not primary products of sonolysis.

Introduction

Most of the chemical reactions, which are brought about in aqueous solutions by ultrasonic waves intense enough to produce cavitation, are oxidations. For example, iodine is formed in a solution of potassium iodide insonated under an atmosphere of argon.¹ However, the reverse reaction, i.e., the reduction of iodine, is observed if the argon atmosphere contains some hydrogen. This effect was explained by the generation of free hydrogen atoms in the cavitation bubbles.² More recently, H atoms have been detected in the insonation of aqueous solutions of the spin trap DMPO (5,5-dimethylpyrroline N-oxide) under argon.

In the present paper, reduction reactions were studied that occur in the insonation of solutions containing solutes which are known to react very rapidly with hydrogen atoms. These studies were complemented by ESR measurements on insonated solutions of DMPO. The initial distribution of the H atoms generated by ultrasound is quite inhomogeneous and even heterogeneous. The atoms are formed in adiabatically compressed cavitation bubbles. Temperatures of several 1000 K and pressures of several 10 bar are believed to exist in these bubbles.⁴⁻⁶ Under these circumstances two kinds of H atom reactions seem to be possible. Solutes with a high vapor pressure may react with the H atoms in the gaseous cavitation bubbles. Solutes, which cannot readily enter the gas phase, react with the few H atoms that reach the liquid phase. As the local concentration of radicals or atoms at the interface is very high, a solute has to be very reactive toward H atoms in order to scavenge them before they react with each other.

Anbar and Pecht⁷ have already pointed out that volatile scavengers such as propanol-2 may undergo reaction in the hot cavitation bubbles. In a more recent study on the scavenging of OH radicals it was found that the efficiency of various solutes did not parallel their specific rates of reaction with OH in homogeneous solution.⁸ In fact, the ability of a scavenger to be

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accumulated in a cavitation bubble or in the interfacial region between the bubble and the liquid seemed to be the determining factor for the scavenging efficiency. The present work was done to find out whether similar factors influence the efficiency of H-atom scavenging.

It has occasionally been proposed^{9,10} that hydrated electrons might be generated in cavitation bubbles. Hydrated electrons are also formed when H atoms are generated in strongly alkaline solutions as the pK value of the equilibrium

$$H + OH^{-} \rightleftharpoons H_2O + e_{aa}^{-}$$
(1)

is 9.8.¹¹ To distinguish between reactions of e_{aq}^{-} and H one has to use a solute which reacts with the two species with substantially different specific rates. In the present work, Tl⁺ ions were used which are known to react very rapidly with e_{aq}^{-} ($k = 3 \times 10^{10}$ M⁻¹ s⁻¹)¹² and relatively slowly with H ($k = 1.2 \times 10^8$ M⁻¹ s⁻¹).¹³

Anbar and Pecht¹⁴ detected H atoms in the sonolysis of aqueous solutions of deuteriated formate by measuring the yield of HD: $H + DCO_2^- \rightarrow HD + CO_2^-$. They found that the HD yield was about 50 times lower than the H_2 yield and independent of the formate concentration in the range from 0.025 to 0.1 M. Formate is a very inefficient scavenger for sonolytically generated radicals as it is not readily accumulated in the interfacial region of a cavitation bubble;⁸ moreover, its specific rate of reaction with H atoms is rather low $(2.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-113})$. The scavengers used in the present study are much more reactive toward H atoms. In the work of Anbar and Pecht, it was also observed that the HD yield became lower in strongly alkaline solutions. This was explained by the conversion of H atoms into hydrated electrons, the latter being nonreactive toward formate.

Experimental Section

Apparatus and Chemical Analysis. The 1-MHz generator and insonation vessel have been described previously.^{15,16} The solution

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Figure 1. Relative radical yield as a function of the composition of the argon-hydrogen atmosphere. Concentration of DMPO: 8×10^{-3} M. Insonation time: 30 s.

was deaerated by bubbling with the argon-hydrogen mixture for 20 min. During the insonation the vessel was closed. A 30-cm³ volume of the solution was irradiated, the total volume of the vessel being 135 cm³. At the intensity of 2 W/cm² of the ultrasonic field the surface of the solution was strongly agitated, and in this way an efficient gas exchange between the solution and the atmosphere was established. The vessel had two side arms carrying 1-cm and 0.2-cm cuvettes. The formation of some products could thus be followed by spectrophotometric measurements without opening the vessel.

Silver metal was formed as a colloid in the Ag⁺ ion containing solution. A drop of tetranitromethane was added to the insonated solution and the concentration of the aci-nitroform anion determined by its absorbance at 350 nm ($\epsilon = 1.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$):

$$Ag + C(NO_2)_4 \rightarrow Ag^+ + C(NO_2)_3^- + NO_2 \qquad (2)$$

The stoichiometry of reaction 2 was checked by reacting tetranitromethane with a silver colloid of known concentration prepared by radiolytic reduction of Ag⁺.¹⁷

Colloidal gold metal was formed in the NaAuCl₄-containing solution. The disappearance of AuCl₄ was measured by following the absorption changes at 270 nm. AuCl₄⁻ reacts thermally with H_2 , the rate of this reaction being substantially lower than that of the sonolytic reaction. The results were corrected for the thermal contribution.

The reduction of I2 in KI solution was followed by measuring the decrease in the 350-nm absorption of the I_3 anion. Br_2 concentrations were determined by adding 10⁻² M NaI to the insonated solution and measuring the absorption of the I2 formed.

MnO₂ was formed as a colloid in the insonation of solutions containing potassium permanganate. Knowing the absorption coefficient of this colloid ($\epsilon = 9 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ at 340 nm),¹⁸ the amount of MnO₂ formed could readily be determined. The colloidal solution was transparent and practically not opalescent which indicates that very small colloidal particles were formed (<100 Å).

Thallium metal was formed as a colloid in alkaline solutions containing TlClO₄. The amount of thallium was determined spectrophotometrically at 500 nm where most of the attenuation of the light beam was due to scattering. An absorption coefficient of 2.9 \times 10³ M⁻¹ cm⁻¹ was determined by producing a known amount of the colloid radiolytically.¹⁹

ESR Measurements. The ESR spectrum of the 8.4×10^{-3} M DMPO solution was measured shortly after sonication at ca. 20 °C in a flat quartz cell with a Varian E-9 spectrometer equipped with an E-232 dual cavity (X-band, 100-kHz field modulation). The spectrum contained the signals for both the OH and H adducts of DMPO. The H adduct was not stable. Its concen-





Figure 2. H₂O₂ yield in the insonation of water under argon-hydrogen mixtures.



Figure 3. Rate of reduction as a function of the composition of the argon-hydrogen mixture for three H atom scavengers.

tration was determined from the double integral of the ESR spectrum relative to the signal intensity of a ruby secondary standard placed in one of the compartments of the dual cavity. The secondary standard was calibrated by comparison with the first moment of the ESR spectrum of aqueous MnSO₄.²⁰ The second-order rate constant for the decay of the H adduct was 2k= $(9 \pm 1) \times 10^2$ M⁻¹ s⁻¹, in good agreement with the value of 7.0 \pm 1.5) \times 10² M⁻¹ s⁻¹ reported by Kalyanaraman et al.²¹ The DMPO-H concentration given in the present work refers to the time of termination of sonolysis and was obtained by extrapolation according to the second-order rate law. The DMPO was obtained from Aldrich and purified over charcoal.

Results

Spin-Trapping Experiments. Figure 1 shows the relative intensity of the signals of both the H and OH adducts of DMPO as functions of the concentration of H₂ in the argon-hydrogen atmosphere. The absolute concentration of the H adduct formed during 30-s insonation under pure argon was 2×10^{-6} M. While the signal of the OH adduct decreased very rapidly with increasing H_2 concentration, that of the H adduct decreased more slowly. Hydrogen peroxide is known to be formed by the combination of OH radicals. Figure 2 shows that the yield of H_2O_2 decreases as more and more H_2 is present in the atmosphere under which water is insonated. These experiments show that OH radicals are practically no longer important at H2 concentrations above 20 vol % and it was therefore expected that reduction processes would best be achieved in the irradiation of solutions under an atmosphere of 80% Ar:20% H₂.

Inorganic H Atom Scavengers. Figure 3 shows that the yield of reduction of various solutes passes through a maximum at 15-30 vol % H₂. The rate of reduction of five solutes is plotted in Figure 4 as a function of solute concentration, the gas atmosphere having

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Figure 4. Rate of reduction as a function of the concentration of various H atom scavengers. Gas: 80 vol % Ar:20 vol % H₂.

TABLE I: Efficiency of Solutes for H Atom Scavenging in Sonolysis and in Homogeneous Solution

scavenger	rel eff in sonolysis	specific rate in homogeneous soln, ¹² M ⁻¹ s ⁻¹	rel eff in homogeneous soln
Br ₂ in KBr soln	1	4.2×10^{10}	1
I ₂ in KI soln	0.35	2.3×10^{10}	0.55
MnO₄⁻	0.20	2.8×10^{10}	0.66
AuCl_	0.08	5.7×10^{9}	0.13
Ag ⁺	0.03	1.1×10^{10}	0.26

a composition of 80 vol % argon and 20 vol % hydrogen. The concentrations are expressed as gram-equivalents per liter and so the results of the various solutes, which require different equivalents of reduction, are comparable. In all cases studied, the yield was proportional to the irradiation time. In Table I are listed (1) the relative efficiency of scavenging in sonolysis as calculated from the rate at a solute concentration of 10^{-3} M and putting the yield for the reduction of Br_2 equal to one, (2) the absolute rate constants for reaction with the H atom, 13 and (3) the relative efficiency of scavenging in homogeneous solution as calculated from these rate constants. Although Br_2 is the most efficient scavenger in both sonolysis and homogeneous solution experiments, there does not seem to exist a correlation between the two efficiencies for the other solutes. The rate of formation of H_2O_2 under pure argon is 3.5×10^{-5} g-equiv $\cdot 1^{-1}$ ·min⁻¹ (Figure 2). Some of the rates in Figure 3 are substantially higher, which shows that reduction processes can be initiated sonolytically with rather high yields.

Hydrated Electron Scavenging with Tl^+ . The nature of the colloid formed in the insonation of a 0.25 M TiClO₄ solution depends on whether hydrogen is present in the argon atmosphere or not. Under pure argon, a reddish colloid is produced which after a while precipitates as Tl(OH)₃; i.e., under these conditions the Tl⁺ ions are oxidized. In the presence of 20 vol % H₂ in the gas atmosphere, no coloring of the solution takes place unless it contains an appreciable concentration of NaOH. The colloid formed in strongly alkaline solution has a grey color. It precipitates at longer irradiation times. It slowly dissolves upon contact of the insonated solution with air or after addition of a drop of hydrogen peroxide. We conclude that the presence of hydrogen in the gas atmosphere and a high OH⁻ concentration are necessary to achieve sonolytic reduction of Tl⁺.

Figure 5 shows how the rate of thallium formation depends on the composition of the gas atmosphere. It is again observed that the yield decreases at high hydrogen concentrations. The dependence of the Tl concentration on the time of irradiation is shown in Figure 6 for a solution containing 0.25 M TlClO₄ and different concentrations of NaOH. The curves bend slightly toward the horizontal axis at longer irradiation times which is due to an artifact caused by the partial precipitation of the colloid. Rates were calculated from the initial slope of the curves. In Figure 7 the rate of Tl formation is plotted as a function of the Tl⁺ concentration, the concentration of NaOH being 1 M. It is seen that the rate strives toward a limiting value at higher Tl⁺ concentrations.



Figure 5. Rate of thallium formation as a function of the composition of the argon-hydrogen atmosphere. $[TlClO_4] = 0.25 \text{ M}, [NaOH] = 1 \text{ M}.$ Dashed line: $Tl(OH)_3$ formation besides Tl.



Figure 6. Concentration of thallium as a function of the insonation time. $[TlClO_4] = 0.25$ M. Various concentrations of NaOH. Gas: 80 vol % Ar:20 vol % H₂.



Figure 7. Rate of thallium formation as a function of the concentration of TlClO₄. Gas: 80 vol % Ar:20 vol % H₂. [NaOH] = 1 M.

Discussion

The primary step in the sonolysis of water under argon is the dissociation 1,3,7,10

$$H_2O \rightarrow H + OH$$
 (3)

When H₂ is present in the gas bubbles, OH radicals are scavenged

$$OH + H_2 \rightarrow H_2O + H \tag{4}$$

explaining why less OH radicals reach the interface to react with DMPO or form H_2O_2 (Figures 1 and 2). In the presence of H_2 , more H atoms should be formed, and one would expect to increase in the yield of the DMPO-H adduct and in the reduction of solutes. However, a gradual decrease in the yield of the adduct was observed (Figure 1). A satisfactory explanation for this effect cannot be given. It should be emphasized that the concentration of the DMPO-H adduct is about 10 times smaller than the concentrations of the reduction products of other solutes; i.e., scavenging of H atoms by DMPO is a very inefficient process and one should perhaps not attach too much significance to the exact

shape of the yield vs H_2 concentration curve in Figure 1.

In the case of the other solutes, maxima in the yield vs H_2 concentration curve are observed (Figure 3). With increasing H_2 concentration, more OH radicals are scavenged that would otherwise reoxidize the reduction products formed by H atom attack on the solutes. However, with increasing concentration of the diatomic H_2 in the cavitation bubbles, the temperatures reached in the adiabatic compression phase are lower. These two opposing effects make one understand that the yield vs H_2 concentration curves pass through a maximum.

Whether a net oxidation or reduction of a solute occurs when a solution is irradiated under argon, where both OH and H are formed, depends on the specific rates of reaction with these radicals. In addition, the product of reduction may be reoxidized by the H_2O_2 formed. In the case of Tl⁺ the oxidation prevails which is understood in terms of the much greater reactivity of Tl⁺ toward OH²² than H.¹³ In the case of Ag⁺, which reacts a little faster with H than with OH, a small reduction is observed (Figure 3). AuCl₄⁻ is consumed at a higher rate than Ag⁺ under argon. This indicates that the product of the reaction of H atoms with this solute is not efficiently reoxidized by the OH radicals or H_2O_2 .

The fact that the efficiencies for scavenging in sonolysis and in homogeneous solution (Table I) cannot be correlated shows that another factor influences the effective reactivity of a solute toward H atoms generated in sonolysis. One thus encounters a situation similar to that in OH scavenging experiments in sonolysis.⁸ In these studies, the decrease in the yield of H_2O_2 under pure argon was measured by using various organic solutes as OH scavengers. It was found that the efficiency depended on the hydrophobicity ratio of the solute (ratio of the number of hydrophobic to hydrophylic groups in a molecule), and this result was interpreted in terms of an accumulation of solute molecules in an interfacial region where the OH radicals form H_2O_2 . It is conceivable that bromine and iodine, which are the most efficient H atom scavengers in sonolysis, can move more readily into the interfacial region or even into the gas phase of the cavitation bubbles than the other scavengers in Figure 4. Among these scavengers, the cation Ag⁺ is more strongly solvated than the others and more likely to stay in solution and not reside in the interfacial region or even be sputtered into the gas phase.

Solutes which cannot enter the gas phase are oxidized or reduced with rates of the order of 10^{-5} M·min⁻¹, while reactions in the gas phase often occur with rates 10-100 times higher. For example, N₂O is decomposed in argon bubbles with a rate of a few 10^{-4} M·min^{-1,23} Such high rates are observed in Figure 4 for bromine and iodine. The curves for these two scavengers show typical saturation characteristics. It seems that all the H atoms generated in a cavitation bubble are scavenged at the higher concentrations. These two solutes are mainly present in the complexed forms Br_3^- and I_3^- . Possibly, at the higher temperatures in the interfacial region, the equilibria $I_3^- \rightleftharpoons I_2 + I^-$ and $Br_3^- \rightleftharpoons I_2$ molecules to evaporate into the gas phase at an appreciable rate.

Thallium ions are not reduced in neutral or weakly alkaline solutions where the equilibrium of eq 1 lies on the left side (Figure 6). Rather high OH^- concentrations of about 1 M are necessary to bring about the reduction. It is concluded that only hydrated electrons have a chance to reduce TI^+ ions under the conditions of sonolysis

$$\mathbf{e}_{ao}^{-} + \mathbf{T}\mathbf{l}^{+} \to \mathbf{T}\mathbf{l}^{0} \tag{5}$$

as the H atom reaction

$$H + Tl^+ \rightarrow H^+ + Tl^0 \tag{6}$$

is too slow to be able to compete with the fast combination

$$\mathbf{H} + \mathbf{H} \to \mathbf{H},\tag{7}$$

which takes place in the interfacial region. That pH values far above the pK of the equilibrium of eq 1 are required is understood in terms of the rather slow specific rate of the forward reaction of this equilibrium ($k = 1.40 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$). The conversion of H atoms into e_{aq}^- (eq 1) has to compete with the combination of the H atoms (eq 7). At [OH⁻] = 1 M, where an appreciable rate of Tl⁺ reduction is observed (Figures 6 and 7), the rates of reactions 1 and 7 are approximately equal, i.e., $k_7[\text{H}]_i = k_{1f}$ [OH⁻] (where $k_7 = 1.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ is the specific rate of reaction 7, [H]_i the local concentration of the H atoms in the interfacial region, and k_{1f} the rate constant of the forward reaction of eq 1).

One thus calculates a local H atom concentration of about $1.4 \times 10^7/1.5 \times 10^{10} = 10^{-3}$ M, and a lifetime of the H atom with respect to reaction 7 of roughly 10^{-7} s. Hydrated electrons, formed via reaction 1 also are very short-lived as they may react either with each other or H atoms in the interfacial region. A rather high Tl⁺ concentration is therefore required to scavenge the electrons efficiently (Figure 7).

Another important conclusion which may be drawn from the observations on the reduction of Tl⁺ ions is that hydrated electrons are not formed directly in the cavitation bubbles, since no Tl⁺ reduction was observed in neutral or slightly alkaline solutions. This result seems to be in contrast to a finding by Margulis and Mal'tsev⁹ who reported on the formation of Cl⁻ in the sonolysis of chloroacetate solutions. Only e_{aq}^- attack on ClCH₂COO⁻ leads to Cl⁻, while H atoms produce H₂. They found an increase in Cl⁻ concentration at high pH values which is understood in terms of e_{aq} formation from H atoms. However, they also observed a small amount of Cl⁻ in the insonation of neutral solutions and interpreted this finding as a proof of the direct formation of hydrated electrons in cavitation bubbles. This proof is not unambiguous as it is known that organic solutes are decomposed not only by free-radical attack in sonolysis (indirect action) but also by a second mechanism which involves the high temperatures in the interfacial region (direct action).^{7,15} The splitting of the Cl-C bond in chloroacetate by this second mechanism cannot be excluded.

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