| water content (H ₂ O/SO ₃ H) | $D_{\text{chem}},$ $10^6 \text{ cm}^2/\text{s}$ | water content (H ₂ O/SO ₃ H) | $D_{\text{chem}},$ 10 ⁶ cm ² /s |
|---|--|---|--|
| 2 | 1.3 | 6 | 2.0 |
| 3 | 4.2 | 9 | 1.7 |
| 4 | 2.3 | 14 | 1.5 |

indicates no immobile water at low membrane water contents since no very broad components are observed in the spectrum. Thus, we conclude that, in the extreme of low water content, H_2O and H⁺ probably diffuse by an identical mechanism, i.e. that the mobile species under an electric field is solvated H⁺, of mobility identical with that of H_2O . At such low water levels in the membrane, all ¹H nuclei would thus diffuse together and the measured diffusion coefficient of ¹H is, again, a good estimate of the water diffusion coefficient in the membrane. Thus, on the basis of the above arguments for high and for low water contents, we tentatively identify the ¹H diffusion coefficient measured here as the intradiffusion coefficient of H_2O in the membrane over the entire range of membrane water contents. We are, however, planning experiments employing $H_2^{17}O$ to provide definitive water diffusion coefficients in order to further substantiate this point.

In a real membrane in which a water concentration gradient exists, such as in an operating fuel cell, diffusion of water through the membrane takes place in a chemical potential gradient. Flux as described by Fick's law is generally relative to a concentration gradient, i.e.

$$flux = D_{chem}(dC/dx)$$
(2)

Conversion of a measured intradiffusion coefficient to a "chemical" diffusion coefficient is carried out using the equation

$$D_{\rm chem} = \left(\frac{\mathrm{d}\,\ln\,a}{\mathrm{d}\,\ln\,C}\right) D^* \tag{3}$$

where D_{chem} is the "chemical" diffusion coefficient, D^* is the intradiffusion coefficient, a is the activity of the diffusing species,

and C is the concentration of the diffusing species (i.e. the membrane water content). The "chemical" diffusion coefficients are obtained by use of eq 3 and the isopiestic data shown above. The curve shown in Figure 3 is transformed into a plot of $\ln a_{water}$ vs ln C_{water} . This curve is next fit to a third-order polynomial, and the derivative term in eq 3 is then directly obtained. The calculated values of D_{chem} show a much smaller range of variation with water content than do the self-diffusion coefficients (Table III). This is caused mainly by the much stronger variation of water activity with water content at the lower water contents studied, as can be seen in Figure 3. The large variations of the activity coefficient of water at low water contents provide an additional "drive" for water transport, compensating for the large drop in the value of the intradiffusion coefficients.

This report demonstrates the capability of the NMR technique to provide the desirable information of diffusion coefficients of water (¹H) in PEFC membranes maintained at a well-defined state of partial hydration. More extensive work is currently in progress in our laboratory to determine diffusion coefficients of water in Nafion and other ionomeric membrane systems under a variety of conditions, most importantly, elevated temperatures. PGSE measurements on hydrated Nafion membranes employing ¹⁷O as the probe nucleus will be carried out to directly ascertain the diffusion coefficient of water in the membrane. As suggested above, the results described in this communication are currently being applied in the development of a water transport model for polymer electrolyte fuel cell systems.¹⁷

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Radical Scavenging in the Sonolysis of Aqueous Solutions of I⁻, Br⁻, and N₃⁻

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Iodide and bromide solutions are sonolyzed under pH conditions, where reactions of the products, i.e. hydrogen peroxide and iodine (or bromine), do not occur. The total yield of the products as well as the hydrogen yield is independent of solute concentration. The results are understood in terms of the competition of the OH + OH and the OH + solute reactions. A local concentration of 4×10^{-3} M of the OH radicals in an interfacial region between the cavitation bubbles and the liquid is derived from the data obtained. The sonolysis of azide solutions is also investigated. The main product is nitrogen, which is formed in the reaction of N_3^- with OH radicals in the millimolar concentration range. At higher azide concentrations, additional nitrogen is formed as hydrogen atoms are also scavenged. Ammonia and hydrazine are minor products of the N_3^- sonolysis.

Introduction

The kinetics of chemical reactions that are initiated by ultrasound are rather complex.¹⁻⁴ The reactions do not take place homogeneously in the solution but in "hot-spots" where cavitation bubbles pulsate or collapse. During the adiabatic compression phase in such gas bubbles, temperatures of several 1000 K are reached and pressures of up to 100 bar. Molecules can be dis-

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Sonolysis of I⁻, Br⁻, and N₃⁻ Solutions

sociated in the hot gas bubbles. Water vapor, for example, is decomposed to yield H atoms and OH radicals and a small amount of oxygen atoms. About 10% of these intermediates reach the liquid phase where they can react with solutes. These reactions generally do not occur homogeneously in the solution as the radicals are present in an interfacial region at a high local concentration, which favors their mutual deactivation. Rather high solute concentrations are therefore required to scavenge the radicals efficiently.

One of the most frequently studied sonochemical reactions is the oxidation of iodide ions which leads to $I_3^{-5.6}$ This reaction also occurs in the absence of oxygen, for example, when an aqueous KI solution is sonicated under an atmosphere of argon. The oxidation of iodide is attributed to the action of OH radicals formed in the argon cavitation bubbles which reach the liquid phase:

$$H_2O \rightarrow H + OH$$
 (1)

$$OH + I^- \rightarrow OH^- + I \tag{2}$$

$$2I + I^- \rightarrow I_3^- \tag{3}$$

It has been shown in our previous work that hydrogen peroxide is also a product of the sonolysis of KI solutions.⁶ It is formed by the combination of OH radicals which have reached the liquid phase:

$$2OH \rightarrow H_2O_2$$
 (4)

In the present paper, the iodine and hydrogen peroxide yields are reexamined to prove more quantitatively the competition mechanism of reactions 2 and 4. Such a reexamination was necessary as in all the previous work on iodide oxidation one has neglected the fact that the products, i.e. H_2O_2 and I_3^- , react in neutral or alkaline solutions according to^{7,8}

$$H_2O_2 + I_3^- \rightarrow 3I^- + O_2 + 2H^+$$
 (5)

Slightly acidic buffered solutions of KI were used in the present study. Similar experiments were carried out on the oxidation of Br^{-} using solutions at pH = 3.0.

The sonolysis of NaN₃ solutions was also investigated. The azide anion, which in many respects resembles the halide anions, is oxidized by the OH radical to yield N_2 . However, as the azide anion is also reactive toward the H atom, additional products and much more nitrogen is formed than expected from the OH yield.

Experimental Section

The irradiation setup has been described previously.⁹ Solutions of 25-cm³ volume were irradiated by 1-MHz ultrasound. Before irradiation, the desired gas or gas mixture was bubbled through the solution. During irradiation, the vessel was closed. The vessel had a side arm equipped with a 1-cm quartz cuvette to allow optical absorbance measurements after various times of irradiation without exposing the solution to air. The vessel also had a side arm with a septum for injecting analytical reagents or for extracting gaseous or liquid samples with a syringe, again without bringing the solution into contact with air.

The iodine concentration in the irradiated solutions was determined spectrophotometrically (the absorption coefficient of I₃⁻ at 350 nm being $2.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). In the case of the iodide solutions of lower concentration, 1 mL of 2.5 M KI solution was injected before the optical measurement to ensure that the I₂ was quantitatively converted into I_3 . H_2O_2 was subsequently determined by adding 60 μ L of a 5 × 10⁻² M ammonium molybdate solution and measuring the increase in the 350-nm absorbance. This absorbance was corrected for the small contribution due to the ammonium molybdate itself. All the iodide solutions contained



Figure 1. Rates of iodine and hydrogen peroxide formation as functions of the iodide concentration. Sonication under argon. Sonication time was 20 s.



Figure 2. Rates of bromine and hydrogen peroxide formation as functions of the bromide concentration. Sonication under argon. Sonication time 20 s; pH 3.0, adjusted with HClO₄.

phosphate buffer and had a pH of 5.9.

Br₂ in the sonicated bromide solutions was determined by adding 1 mL of 2.5 M KI solution and measuring the absorbance produced by the iodine formed. The H_2O_2 concentration was then determined as described above. All the bromide solutions had a pH of 3.0 (adjusted with HClO₄) to prevent any reaction between the products, i.e. Br_2 and H_2O_2 .

 N_2 and H_2 produced in the sonication of NaN₃ solutions were determined gas chromatographically. Hydrogen peroxide was determined spectrophotometrically after the addition of potassium iodide and ammonium molybdate. Ammonia was determined with a cation chromatograph (Dionex type 2010; column, HPIC-CS2; eluent, 0.005 M HCl). As sodium disturbed the determination of ammonia, CsN₃ solutions were sonicated in these experiments. CsN_3 was prepared from commercial $Ba(N_3)_2$ and Cs_2CO_3 .

Results

Figure 1 shows the rates of iodine and hydrogen peroxide formation as functions of the iodide concentration. The sum of the two rates is also shown. This sum is constant within the 10% reproducibility of the data. It was found that the yield of hydrogen was also independent of the iodide concentration (this yield being about 5% greater than that of hydrogen peroxide as small amounts of oxygen are produced in the sonolysis of water⁶).

Similar results were obtained in the oxidation of bromide. Figure 2 shows the rates of bromine and hydrogen peroxide formation. The formation of bromide was also investigated by sonicating a 2.5 M KBr solution under argon-oxygen atmospheres of various composition. Figure 3 shows the bromine concentration as a function of time. It can be seen that the oxidation of bromide proceeds a little faster under pure oxygen than argon. However, in the presence of mixtures of the two gases, substantially greater yields are observed. For example, when a mixture containing 42% oxygen is used, the rate of bromine formation is about 10 times greater than under pure argon. Similar effects have been observed previously for the oxidation of iodide.⁶

Figure 4 shows the rate of formation of various products from the sonication of sodium azide solutions at various N_3^- concen-

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Figure 3. Bromine concentration as a function of time in the irradiation of a 2.5 M KBr solution under argon-oxygen mixtures of various composition.



Figure 4. Rate of formation of various products from the sonolysis under argon at variable azide concentrations. The sonication time was 10 min for the determination of the gases and 1 min for the determination of hydrogen peroxide.

trations up to 2 M. Nitrogen is known to be formed in the reaction of OH radicals with azide anions:¹⁰

$$OH + N_3^- \rightarrow OH^- + N_3 \tag{6}$$

$$2N_3 \rightarrow 3N_2 \tag{7}$$

Three molecules of N_2 are produced per two OH radicals consumed (or one less molecule of H_2O_2 is formed). It can be seen from Figure 4 that the N_2 yield increases steeply in the millimolar concentration range where the H_2O_2 yield decreases substantially. Above an azide concentration of 0.005 M, the yield continues to increase, although the slope of this increase is almost 10 times smaller than at the beginning. The nitrogen yield finally approaches a limiting value at azide concentrations above about 0.1 M. The hydrogen yield decreases with increasing azide concentration, this decrease being slower than that of the hydrogen peroxide yield. It is known that the azide anion can react with hydrogen atoms:¹⁰

$$H + N_3^- \rightarrow NH^- + N_2 \tag{8}$$

$$NH^- + H_2O \rightarrow NH_2 + OH^-$$
(9)

$$NH_2 + N_3^- \rightarrow NH_2^- + N_3 \tag{10}$$

$$N_3 \rightarrow 1.5 N_2 \tag{11}$$

$$H_2O \rightarrow NH_3 + OH^-$$
 (12)

net:
$$H + 2N_3^- + 2H_2O \rightarrow NH_3 + 2.5N_2 + 2OH^-$$
 (13)

NH₂

A lot of additional nitrogen is formed in this sequence of elementary reactions. If N_3^- scavenged H atoms which would otherwise yield H_2 , $2NH_3$ and $5N_2$ molecules would be formed for each H_2 molecule not formed.

It was observed during the H_2O_2 determinations using the above iodide method that the iodine produced faded away, especially for azide solutions with a concentration higher than 0.01 M. It has to be concluded that sonication of these solutions produces an additional product which is oxidized by iodine. Hydrazine seems to be a possible candidate having such reducing properties. In fact, it was found that hydrogen peroxide solutions containing small amounts of hydrazine sulfate showed the same instability upon analysis by the iodide method. From the rate of iodine decrease in such solutions it can be concluded that the rate of sonolytic hydrazine formation at an azide concentration of 0.1 M is roughly 3×10^{-5} M min⁻¹.

Discussion

Oxidation of I⁻ and Br⁻. The results obtained with the iodide and bromide solutions reveal two important facts: (1) The total yield of oxidized products, i.e. H_2O_2 and I_2 (or Br_2), is independent of the solute concentration and equal to the hydrogen peroxide yield in pure water (Figures 1 and 2). (2) The hydrogen yield is not influenced by these solutes. The two solutes are known to be nonreactive toward H atoms in aqueous solution. Nevertheless, one might have suspected that some of the intermediate H atoms, before forming molecular hydrogen, could have reduced I_2 (or Br_2) formed by the action of OH on iodide (or bromide).

The amount of hydrogen peroxide formed decreases with increasing I⁻ or Br⁻ concentration, and the amount of oxidized solutes increases correspondingly. One can understand this in terms of a constant amount of OH radicals reaching the aqueous phase. Once in solution, they can undergo reactions among themselves (eq 4) or with a solute (eq 2). At the iodide concentration of 5×10^{-3} M, the hydrogen peroxide yield is decreased by 50%. This value of the half-concentration of iodide is very much lower than that obtained in the previous studies where reaction 5 had been neglected.^{5,11} (Under the pH conditions of these previous studies, iodine was found only at iodide concentrations where the amount of I₂ generated exceeded that of H₂O₂. As a consequence, the half-concentration of iodide was about 2 orders of magnitude higher than the true one.) At the half-concentration of iodide the rates of the reactions of eqs 2 and 4 are equal:

$$k_2[I^-][OH] = 2k_4[OH]^2$$
 (14)

Using $k_2 = 1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and $2k_4 = 1.2 \times 10^{10} \text{ }^{12}$ one calculates an approximate local OH concentration of 4×10^{-3} M in the interfacial region.

We thus conclude that the OH radicals hardly escape into the bulk solution. The situation is especially serious because of the high specific rate of the OH + OH reaction. If the OH radicals, in their reaction with a solute, form secondary radicals, which have a substantially lower rate of mutual deactivation, these secondary radicals can migrate much more easily into the solution and can be scavenged by a second solute at relatively low concentration. A typical example is the scavenging of OH radicals by formic acid which has been described previously; again high concentrations of HCOOH are required to scavenge the OH radicals efficiently.^{6,13} The CO₂^{\sim} radicals formed in the OH + HCOOH reaction interact among each other with a specific rate much lower than k_4 . They can therefore diffuse into the bulk solution and be scavenged efficiently by oxygen present at low concentration, the product of the $CO_2^- + O_2$ reaction being long-lived O_2^- in alkaline solution.⁶ Sonochemical reactions in aqueous solutions often resemble radiation chemical reactions which are initiated by γ -rays. However, the OH radicals generated by γ -irradiation are almost homogeneously distributed in solution, and therefore much

⁽¹¹⁾ Reference 6, see Figure 2.

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lower scavenger concentrations are usually required than in sonolysis studies.

The specific rate of the reaction of OH with Br⁻ is about the same as that of the OH + I^- interaction.¹² The Br⁻ concentration at which the H_2O_2 yield is decreased by 50% is therefore close to the half-concentration of I⁻. The remarkably high yield of bromide oxidation in the presence of both argon and oxygen (Figure 3) is understood in terms of two opposing effects which have been described previously in the case of iodide oxidation:⁶ In argon-containing cavitation bubbles the temperatures reached in the adiabatic compression phase are especially high, as argon has a high κ value ($\kappa = C_p/C_v$: the ratio of the specific heats). With increasing oxygen concentration in the gas mixture (oxygen having a lower κ value) the temperature is lower and fewer OH radicals are generated from water vapor. On the other hand, oxygen acts as a scavenger for intermediate H atoms (forming HO₂ radicals) and in this way prevents many OH radicals from recombining with H atoms in the gas bubbles; in addition, oxidizing O atoms are formed in the thermal dissociation of O₂ molecules.

The fact that the hydrogen yield is not affected by the solutes (at least at the low degrees of conversion obtained with the short sonication times used) indicates that intermediate H atoms penetrate less deeply into the liquid than OH radicals. That H atoms are difficult to scavenge by a solute has already been recognized by Anbar and Pecht.¹⁴ However, H atoms can react with hydrophilic solutes when they are produced in argon cavitation bubbles containing 20% H₂; under these circumstances all the OH radicals formed in the gas phase are converted into H atoms via OH + H₂ \rightarrow H₂O + H.¹⁵ It was shown that the local concentration of the H atoms is of the order of 10⁻³ M under these conditions.

Sonolysis of the Azide Anion. Nitrogen is the main product as would be expected from OH attack on N_3^- (eqs 6 and 7). The steepest increase in nitrogen yield with increasing azide concentration occurs indeed in the 10^{-3} M range as in the cases of iodide and bromide. In fact, the specific rate of reaction 6 is comparable to the rates of the corresponding reactions of I⁻ and Br^{-,12} The main decrease in H_2O_2 yield also occurs in the 10^{-3} M azide concentraton range. According to eqs 6 and 7, the yield of N_2 should be 3 times the decrease in the yield of hydrogen peroxide. However, the nitrogen yield is 20% larger than this value, which is attributed to the scavenging of a small amount of hydrogen atoms when the azide concentration is in the millimolar concentration range.

At still greater concentrations (>10⁻² M), the nitrogen yield continues to increase. More and more hydrogen atoms are scavenged here. Two reasons for the more effective scavenging of OH radicals than H atoms can be given. Firstly, the rate constant of reaction with H atoms ($k_8 = 4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-116}$) is smaller than that of the reaction with OH radicals ($k_6 = 1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-112}$). Secondly, and more importantly, the H atoms are scavenged less readily because of their lesser penetration into the aqueous phase as mentioned above. At N₃⁻ concentrations above about 0.5 M, practically all the H and OH radicals that reach the liquid phase are scavenged as the nitrogen yield is close to its limiting value (Figure 4).

Reactions 6-13 can account for 80% of the nitrogen yield. This can be seen from the following material balance at 0.1 M azide concentration: The decrease in H₂O₂ is 3.5×10^{-5} M min⁻¹; the expected N₂ formation by OH radical scavenging is $(3.5 \times 3) \times$ $10^{-5} = 10.5 \times 10^{-5}$ M min⁻¹. The decrease in H₂ production is 2.0×10^{-5} M min⁻¹, the expected N₂ formation by H atom scavenging $(2.0 \times 5) \times 10^{-5} = 10.0 \times 10^{-5} \text{ M min}^{-1}$. The expected total N₂ yield of 20.5×10^{-5} M min⁻¹ is greater than the measured yield of 18.0×10^{-5} M min⁻¹. The NH₃ yield is 2.3×10^{-5} M min⁻¹, which is significantly smaller than the value of (2.3×2) $\times 10^{-5} = 4.6 \times 10^{-5}$ M min⁻¹ expected from the decrease in H₂ yield. The missing nitrogen and ammonia yields have possibly to be explained by side reactions in the mechanism of eqs 8-13. For example, both yields would be decreased if part of the NH₂ radicals (which are generated in a region of high radical density) combined. The fact that evidence for the formation of hydrazine in quantities of some 10⁻⁵ M min⁻¹ was obtained corroborates this explanation.

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