Using the observed value of $7.5 \times 10^7$ cm/s for $Z_{el}$, a bulk concentration of $MG^-$ equal to $6 \times 10^{18}$ molecules/cm$^3$ (an average value from Figure 7) and the upper limit of $6.6 \times 10^{12}$ L/s for $Z_s$, one obtains a coverage of $6.8 \times 10^{13}$ molecules/cm$^2$. The exponential term is taken as unity since, assuming the rate-determining step involves an adsorbed species, the observed free energy of activation is the free energy of activation for the adsorbed reactant. If we assume that one molecule of $MG^-$ occupies 10 Å$^2$, this corresponds to a steady-state fractional coverage of 0.07.

Although this estimated coverage cannot be considered quantitative, it is consistent with the first-order dependence seen for bulk $MG^-$. At higher coverages, saturation of the surface should result in independence of rate on $MG^-$. These conditions, however, are not achieved because a high copper concentration would be needed to maintain kinetic control at the high reaction rates achieved at the high $MG^-$ concentrations required to saturate the copper surface. Clearly, the first-order dependence on $MG^-$ is inconsistant with a saturated coverage of $MG^-$. As previously mentioned, at high concentrations of hydroxide, formaldehyde, and copper, the solution is unstable and formation of copper metal occurs spontaneously in solution.

The change in $Z$ upon substitution of deuterium for protium in formaldehyde is also consistent with cleavage of the carbon-hydrogen bond of an adsorbed $MG^-$ as the rate-determining step. The experimental collision frequencies for formaldehyde and formaldehyde-$d_2$ quoted in the previous section assumed $\kappa = 1$ and $\Delta S^* = 0$ and therefore could be in error by as much as a factor of $10^2$. The relative magnitudes of the two, however, $Z_{CH_2O}/Z_{CD_2O} = 5$ should be correct since it is unlikely that $\kappa$, $\Gamma$, or $\Delta S^*$ change significantly upon isotopic substitution. For example, a difference of 13 J/(mol K) in $\Delta S^*$ would be required to account for the factor of five in the rate. From eq 7, $Z_{el}$ depends only on the molecular weight of the diffusing species. Substitution of deuterium for protium in formaldehyde only reduces $Z_{el}$ by 2%. For an adsorbed species, however, $Z_s$ is related to the vibrational frequencies of the molecule and should be strongly affected by isotopic substitution.

Recently, Evans et al.[21] reported a primary isotope effect $k_H/k_D$ = 3–4 for the oxidation of vrious aldehydes on gold in alkaline solutions. The proposed mechanism was based on a dissociative adsorption step with cleavage of the $\alpha$-carbon–hydrogen bond. Although the electroless process does not appear to be a dissociative adsorption step but rather dissociation following adsorption, the results of Evans seem to be in good agreement with the observations in this study.

## Conclusion

Under conditions where the electroless deposition of copper is kinetically controlled, the reaction is first order in methylene glycolate and zeroth order in all other reactants. Temperature-dependent measurements and isotopic substitution yield an activation energy of 60.9 kJ/mol and a primary kinetic isotopic effect $k_H/k_D = 5$. Indications are that the rate-determining step involves cleavage of a carbon–hydrogen bond of adsorbed methylene glycolate. The acid dissociation constant of methylene glycol has been measured between 40 and 70 °C. $\Delta H$ was found to be 67.2 kJ/mol with a $\Delta S$ of −25.2 J/(mol K).

*Acknowledgment.* We express our gratitude to J. G. Gordon and D. A. Buttry for numerous discussions and support.

**Registry No.** EDTA, 60-00-4; HCHO, 50-00-0; Cu, 7440-50-8; deuterium, 7782-39-0.

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# Free Radical and Free Atom Reactions in the Sonolysis of Aqueous Iodide and Formate Solutions

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Solutions of potassium iodide and sodium formate were irradiated with 300-kHz ultrasound and the products analyzed. The irradiations were carried out under atmospheres of argon, oxygen, and argon–oxygen mixtures of varying composition. In addition, experiments with pure water and water containing ozone were undertaken. The products of irradiation of iodide solutions are iodine and hydrogen peroxide; hydrogen is also formed in the absence of oxygen. With an atmosphere of 70% argon and 30% oxygen, the yields are drastically higher than for irradiation under pure argon or oxygen. The products of the irradiation of formate solutions are hydrogen, carbon dioxide, hydrogen peroxide, and oxalate in the absence of $O_2$ and hydrogen peroxide and carbon dioxide in the presence of $O_2$. A strong enhancement of the yields is also observed for formate solutions containing both argon and oxygen. Ozone could not be identified as a stable product of the irradiation of oxygenated water. On the contrary, water containing ozone was found to rapidly lose $O_3$ upon ultrasonic irradiation. The dependence of the yields of the various products on the concentration of the dissolved substances was studied in order to derive a mechanism of the chemical action of ultrasound. The results are explained in terms of the formation of H and OH radicals in the gas bubbles. In the absence of oxygen, the H atoms form $H_2$ and the OH radicals form hydrogen peroxide or react with nonvolatile substrates in the interfacial region. In the presence of oxygen, $HO_2$ radicals, OH radicals, and O atoms are formed. The $HO_2$ radicals do not attack iodide or formate but produce hydrogen peroxide. Oxygen atoms are scavenged by iodide and formate ions. An appreciable concentration of the superoxide radical anion, $O_2^-$, was detected after the irradiation of an oxygenated, $10^{-2}$ M formate solution of pH 14. The $O_2^-$ anion decayed after irradiation with a half-life of 3 min.

## Introduction

Free radicals such as hydrogen atoms and hydroxyl radicals are known to be generated upon the action of ultrasonic waves on aqueous solutions.[1-4] The chemical effects are brought about in the presence of a monoatomic or diatomic gas. They are due to the high temperatures of several 1000 K and pressures of some 100 bar which exist in the compression phase of oscillating or

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collapsing gas bubbles.[5-7] The radicals from the sonolysis of water vapor in the gas bubbles may react with dissolved substances. In addition to the H and OH radicals formed from water, atoms of diatomic gases, such as oxygen and hydrogen, may be formed in the bubbles, which also participate in the reactions with a solute. Although many papers have appeared, in which the products of radical attack in the sonolysis of aqueous solutions were determined, rather little has been reported on the yields of the radicals and atoms. Further, little is known about the spatial distributions of the radicals in the hot spots where the chemical effects occur.

The radicals may react with volatile solutes in the gas phase or react with dissolved solutes in an interfacial area or even in the bulk solution.[8] In order to obtain information about these reactions, simple redox systems have to be studied, the free radical chemistry of which is known from radiation chemical investigations. In the present paper, we report on the influence of oxygen on hydrogen peroxide formation by studying solutions irradiated under various mixtures of argon and oxygen. The oxidation of iodide, i.e. of a solute which cannot enter the gaseous phase of the hot spots, also is described. This reaction has often been reported in the past, although the elementary processes involved have never been discussed in detail. Finally, we report on the oxidation of formate as a reaction, the mechanism of which has been thoroughly studied in radiation chemistry.

The hot spot chemistry in the sonolysis of aqueous solutions is ruled by rather complex kinetics. In a previous investigation, the inhibition of the $H_2O_2$ formation by various solutes was reported.[9] Hydrogen peroxide is produced via the combination of OH radicals which are formed as the oxidizing intermediate in the irradiation of water under an argon atmosphere. It was observed that the efficiency of an inhibiting solute could not be correlated with its specific reactivity toward OH radicals (as it is known from radiation chemical studies), but the reactivity depended primarily on its hydrophobicity. It was concluded that OH radicals generated in the gas phase form $H_2O_2$ in an interfacial area and that hydrophobic solutes that enter the interfacial area react with the OH radicals and lower $H_2O_2$ yields.

## Experimental Section

The ultrasound was generated by a 300-kHz quartz oscillator. The waves passed through a 1-λ-thick metal plate into a thermostated water bath in which the vessel was fitted at a constant position. The glass vessel had a plane bottom of thin glass in order to minimize sonic absorption and to assure good heat exchange with the water bath. Two kinds of vessels were used: The larger one had a volume of 85 cm$^3$. The volume of irradiated liquid was 55 cm$^3$. A septum was connected to the vessel through which gas samples could be taken out with a syringe. The water-gas interface was 17 cm$^2$, i.e. sufficiently large to allow a strong gas exchange between the two phases (much contact of the irradiated solution with the gas atmospohere is important to obtain reproducible results and good yields). The vessel contained an inlet and outlet for gases or gas mixtures with which the solution was vigorously bubbled during 15 min before irradiation. During irradiation the vessel was closed. The second vessel had a total volume of 66 cm$^3$. The vessel was first purged with the desired gas and then filled with a 56-cm$^3$ solution which had been deaerated by using the syringe techniques described elsewhere.[10] The vessel was also closed during irradiation. Analysis of the gas phase was carried out by transferring the gas into a Van Slyke apparatus. The composition of the gas was investigated with a gas chromatograph. The second vessel was also available with a connection to a horizontally placed pipet of 0.5 cm$^3$ into which a drop of colored water was placed. The formation or consumption of gas during irradiation was followed by measuring the rate of the movement of the drop.

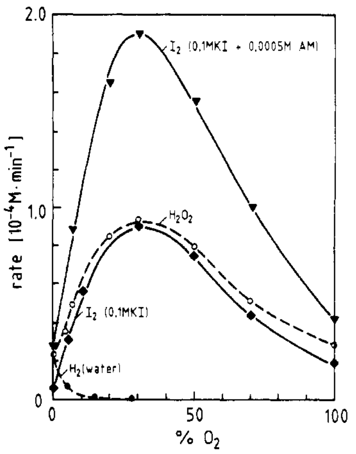

**Figure 1.** Irradiation of water (dashed lines) and of a 0.1 M KI solution (solid lines) under various mixtures of argon and oxygen (the composition of the gas mixture is given in volume percent of $O_2$).

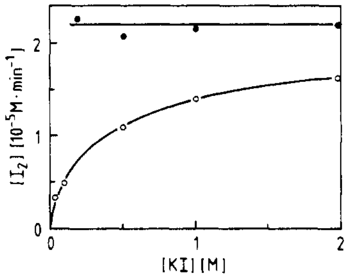

**Figure 2.** Yield of $I_2$ as a function of the KI concentration in the irradiation of solutions under argon in the absence (○) and presence (●) of $5 \times 10^{-4}$ M ammonium molybdate. The rate of $H_2O_2$ formation in pure water was $2.2 \times 10^{-5}$ M min$^{-1}$.

Iodine was determined spectrophotometrically ($\epsilon_{350} = 2.6 \times 10^4$ M$^{-1}$ cm$^{-1}$) and also hydrogen peroxide via its ammonium molybdate catalyzed reaction with iodide. Oxalate was determined with an ion chromatograph. $CO_2$ also was measured with the ion chromatograph in some of the experiments; in others gas chromatography and manometric methods were used. In the latter case, the solutions to be investigated were acidified with sulfuric acid prior to the analysis.

## Results

*Irradiation of Water and Iodide Solutions.* Figure 1 shows the rates of formation of hydrogen peroxide and hydrogen in water irradiated under argon-oxygen atmospheres of different composition (dashed curves). Under pure argon, almost as much $H_2O_2$ is produced as hydrogen. In some experiments, oxygen was also found as a product, the sum of the yields of $H_2O_2$ and $2O_2$ being equal to the $H_2$ yield. In the most extreme case, the $O_2$ yield was 10% of the $H_2O_2$ yield. While the $H_2$ yield was reproducible within 10%, the $O_2/H_2O_2$ ratio changed in an irregular manner. In the discussion, we neglect the formation of $O_2$ as a minor reaction product and formulate a reaction scheme assuming that $H_2$ and $H_2O_2$ are the only products of the sonolysis of water.

The $H_2$ yield in Figure 1 rapidly decreases as oxygen is added to the argon atmosphere. At the same time, the yield of hydrogen peroxide increases. This increase in $H_2O_2$ is much more pronounced than the decrease in $H_2$. The maximum yield of $H_2O_2$ is observed at 30% oxygen in the gas mixture. At higher $O_2$ concentrations, the yield decreases. The hydrogen peroxide yield under pure oxygen is only slightly greater than under pure argon. This dependence of the $H_2O_2$ yield on the composition of the Ar-$O_2$ gas mixture has been reported many years ago.[11]

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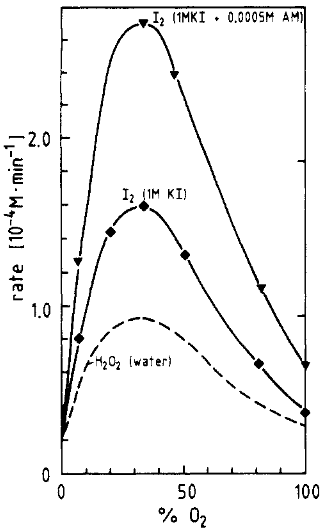

Figure 3. Irradiation of 0.1 M KI solutions (solid lines) under various mixtures of argon and oxygen. The dashed curve gives the $H_2O_2$ yield from water (from Figure 1).

Figure 1 also shows how the iodine yield in the irradiation of a 0.1 M KI solution depends on the $O_2$ concentration of the gas mixture. Under pure argon, less $I_2$ is produced from such a solution than $H_2O_2$ is formed from pure water. This reduction in yield can also be seen from Figure 2, where the $I_2$ yield in the irradiation under an argon atmosphere is plotted vs. the iodide concentration. Rather large $I^-$ concentrations are required to produce $I_2$ in a yield comparable to the yield of $H_2O_2$ in water. In the irradiation of a 0.1 M KI solution under pure oxygen, substantially more $I_2$ is librated than under argon. Maximum $I_2$ yield is again observed for a solution irradiated under an Ar (70%)–$O_2$ (30%) atmosphere (Figure 1).

The $I_2$ yield in Figure 2 strives toward a limiting value at higher iodide concentrations which is lower by 25% than the $H_2O_2$ yield in pure water. This figure also shows the $I_2$ yield in solutions of iodide and $5 \times 10^{-4}$ M ammonium molybdate. In these solutions as much iodine is produced as hydrogen peroxide is produced in pure water. When ammonium molybdate was added after irradiation, the iodine yield did not increase. Ammonium molybdate is a catalyst for the reaction $H_2O_2 + 2I^- \rightarrow I_2 + 2OH^-$, which is too slow in neutral solution to occur under our irradiation conditions. The increase in yield in the presence of the catalyst proves that $H_2O_2$ is a product of the irradiation of KI solutions. In the absence of the catalyst during the irradiation, the $H_2O_2$ formed is catalytically decomposed. (This was checked by adding small amounts of $H_2O_2$ to neutral solutions containing both $I_2$ and $I^-$ and adding ammonium molybdate after a few minutes. Almost no iodine was librated under these conditions.) The $H_2$ yield was not appreciably lowered by KI, and substantial $O_2$ yields were observed in the presence of iodide (resulting from the above-mentioned catalytic decomposition of $H_2O_2$).

In the irradiation of 0.1 M KI solutions under argon–oxygen mixtures, more $I_2$ was liberated when the solutions contained ammonium molybdate during irradiation. The difference in yields between the solutions irradiated with and without the catalyst was roughly equal to the yield of $H_2O_2$ in pure water (Figure 1).

Figure 3 presents the results obtained with a 1 M KI solution. At this higher iodide concentration, the $I_2$ yield under pure argon is greater than in the above 0.1 M solution (Figure 2). In the irradiation under mixtures of argon and oxygen larger yields are observed, too. The dashed line in Figure 3 was taken from Figure 1 to give the $H_2O_2$ yield in water for comparison. Note that the $I_2$ yield under pure oxygen is greater than the $H_2O_2$ yield in the absence of KI.

In Figure 4, the $I_2$ yields obtained at various KI concentrations are plotted for solutions irradiated under argon, oxygen, and the argon (70%)–oxygen (30%) mixture. The curves are normalized for [KI] = 1 M. It is seen that the dependence of the $I_2$ yield on the KI concentration is essentially the same for all three solutions.

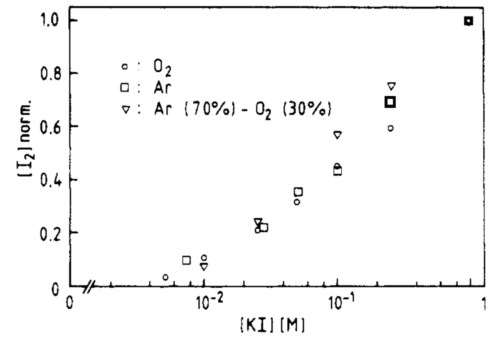

Figure 4. $I_2$ yield as a function of iodide concentration in the irradiation under argon, oxygen, and argon (70%)–oxygen (30%). Yields are normalized for $[I^-]$ = 1 M.

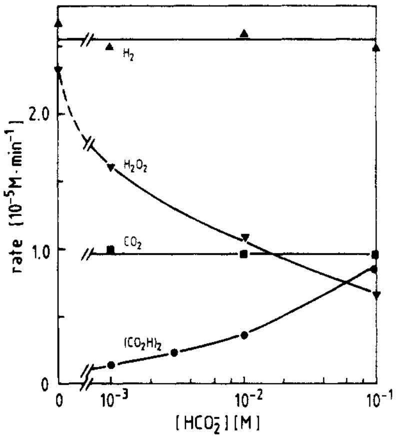

Figure 5. Yields of various products of the irradiation of sodium formate solutions under argon (pH 10).

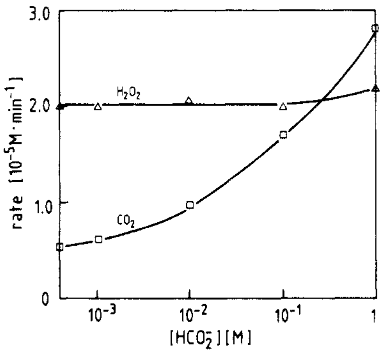

Figure 6. Yields of $H_2O_2$ and $CO_2$ in the irradiation of sodium formate solutions under oxygen.

*Irradiation of Formate Solutions.* The products which are formed in the irradiation of formate solutions under argon and under oxygen are shown by Figure 5 and 6, respectively. Under argon, the yield of hydrogen peroxide decreases with increasing formate concentration. As previously reported, the $H_2O_2$ yield is decreased by 50% at a formate concentration of about $10^{-2}$ M.[9] The hydrogen yield is not changed by the presence of formate. Carbon dioxide and oxalic acid are the products of the oxidation of formate. While the yield of $CO_2$ was practically constant in the investigated range between $10^{-3}$ and $10^{-1}$ M $HCO_2^-$, the oxalic acid yield strongly increased. The sum of the yields of oxalic acid, carbon dioxide, and hydrogen peroxide was equal to the hydrogen yield within the limits of error of the analytical determinations. In the oxygenated solutions, neither hydrogen nor oxalic acid was formed. The yield of hydrogen peroxide was independent of the formate concentration and equal to the yield in pure water. The

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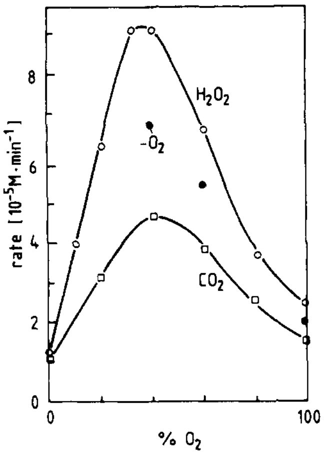

**Figure 7.** Yields in the irradiation of $10^{-2}$ M sodium formate under argon and oxygen mixtures of different compositions.

**TABLE I: Reaction of Formate Ion with Ozone**[a]

| $[HCO_2^-]$, M | $[O_3]$, $\mu$M | pH | $[CO_3^{2-}]$, $\mu$M |
|---|---|---|---|
| 0.001 | 67.4 | 6.32 | 68.6 |
| 0.010 | 67.4 | 6.75 | 67.9 |
| 0.10 | 67.4 | 7.13 | 64.5 |
| 0.001 | 67.4 | 11.84 | 67.6 |
| 0.010 | 67.4 | 12.15 | 65.6 |
| 0.10 | 67.5 | 12.07 | 68.8 |

[a] $[H_2O_2] < 1$ $\mu$M in all runs.

carbon dioxide yield was smaller than in the solutions containing argon at low formate concentrations but became larger at the higher concentrations. Above 0.2 M, the $CO_2$ yield was even greater than that of $H_2O_2$.

Figure 7 shows the dependence of the yields of $H_2O_2$ and $CO_2$ on the concentration of an argon–oxygen atmosphere, under which a 0.01 M formate solution was irradiated. The figure also shows the rate of oxygen consumption. Note that good material balance is achieved as the yield of $O_2$ consumption is half the sum of the yields of $CO_2$ and $H_2O_2$. It is seen that the yields are drastically increased when oxygen is present in the argon atmosphere. Maximum yields again are observed for 30% $O_2$.

*Experiments with Solutions of Ozone.* In an experiment with oxygenated water, $O_2$ was bubbled through the solution. Ozone, if present as a product of irradiation, would be extracted by the stream of oxygen. The effluent oxygen was passed into a KI solution. The optical density of this solution at 350 nm was unchanged during a 10-min irradiation period. A similar treatment with a dilute ozone solution gave a change in optical density. Therefore, it is reasonable to conclude that $O_3$, if it was formed, does not escape the gas bubbles in the same manner as $H_2O_2$ does.

In another experiment, the behavior of $O_3$ during sonolysis was investigated. A 31.8 $\mu$M $O_3$ solution in 1 mN $H_2SO_4$ was sonicated and the $O_2$ content of the gas and liquid phases determined. It was found that 60 s of sonication lowered the $O_3$ concentration to 5.9% of its original concentration. The $O_3$ is at best a transient product during sonolysis. It could, however, be that oxygen atoms from its decomposition can enter the liquid phase.

As formate was used as a scavenger for radicals as described above, it seemed to be interesting to study the reaction of ozone with formate. Thirty milliliters of formate was stirred in a 100-mL syringe while 30 mL of $O_3$ solution was slowly added. The $CO_2$ formed was determined as well as the amount of hydrogen peroxide. The results are compiled in Table I. It is seen that one molecule of $CO_2$ is formed per reacting $O_3$ molecule; $H_2O_2$ is not an accompanying product. The overall reaction is $HCO_2^- + O_3 \rightarrow CO_2 + OH^- + O_2$. One expects an oxygen atom (which as discussed above may be formed in the decomposition of ozone in the gas bubbles) to behave like an ozone molecule, i.e. to react according to $HCOO^- + O \rightarrow OH^- + CO_2$.

*Experiments on the Formation of the Superoxide Radical Anion.* A $10^{-2}$ M formate solution containing 1 M NaOH was irradiated for 2 min under an atmosphere of oxygen. The absorption spectrum was measured immediately after irradiation and its decay followed. The spectrum contained the absorption band with a maximum at 240 nm, which is typical for the superoxide radical anion, $O_2^-$.[12] The lifetime of the radical was about 3 min. Its concentration immediately after irradiation was $3 \times 10^{-5}$ M. When the irradiation of the 1 M NaOH solution was carried out without formate, the radical yield was lower by a factor of 3.

## Discussion

*$H_2O_2$ Yields under Argon and under Oxygen.* H atoms and OH radicals have recently been detected in the sonolysis of water by using an ESR spin trapping method.[4] We therefore formulate the primary process of the sonolytic decomposition of water under an argon atmosphere as

$$H_2O \rightarrow \dot{H} + \dot{O}H \qquad (1)$$

Let the yield of this process be $Y_{Ar}°$. The products $H_2$ and $H_2O_2$ will be formed by combination reactions of the radicals. One has also to discuss a partial recombination of the radicals. If the fraction $f$ of the radicals initially formed recombine

$$f\dot{H} + f\dot{O}H \rightarrow fH_2O \qquad (2)$$

the fractions $(1-f)$ of the radicals will form $H_2$ and $H_2O_2$

$$(1-f)\dot{H} \rightarrow \left(\frac{1-f}{2}\right)H_2 \qquad (3)$$

$$(1-f)\dot{O}H \rightarrow \left(\frac{1-f}{2}\right)H_2O_2 \qquad (4)$$

The fraction $f$ would be 0.5, if all the radical reactions 2–4 occurred with the same specific rate. Under these conditions, both $H_2$ and $H_2O_2$ would be formed with the yield $Y_{Ar}°/4$. However, the H atom reaction 3 (and also reaction 2 to a lesser degree) may be expected to be faster than the OH reaction 4; i.e., the fraction $f$ may be expected to be greater than 0.5. A substantial fraction of recombining radicals from water has also been postulated in earlier work.[13]

In the presence of oxygen, no hydrogen is formed. This is explained by the scavenging of H atoms by $O_2$ in the gas bubbles

$$\dot{H} + O_2 \rightarrow H\dot{O}_2 \qquad (5)$$

followed by

$$H\dot{O}_2 \rightarrow {}^1/_2H_2O_2 + {}^1/_2O_2 \qquad (6)$$

as an additional process that leads to the formation of $H_2O_2$. In spite of this additional process, only slightly more hydrogen peroxide is formed in the irradiation of water under oxygen than under argon. There might be some loss of radicals via the reaction

$$f_1\dot{O}H + f_1H\dot{O}_2 \rightarrow f_1H_2O + f_1O_2 \qquad (7)$$

although one could hardly give any reason why this recombination reaction should be more efficient than the recombination reaction 2 in argon bubbles. A more plausible reason would be a diminished initial yield of decomposed water molecules in the bubbles of the diatomic oxygen, since lower temperatures are expected to be reached than in argon bubbles. The yields of initial water decomposition into radicals under these two gases are roughly related according to

$$Y_{O2}° = Y_{Ar}° \frac{1-f}{2(1-f_1)} \qquad (8)$$

For $f = f_1$, which seems a reasonable assumption, one concludes that water molecules are decomposed at half the rate under oxygen. The occurrence of reaction 7 can be traced by measuring the $^{16}O$–$^{18}O$ exchange in solutions of $^{18}O_2$ in $H_2{}^{16}O$. Experiments of this kind are being carried out in this laboratory.

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In oxygenated water, the dissociation of oxygen molecules

$$O_2 \rightarrow 2O \tag{9}$$

also has to be considered. Under equilibrium conditions, $O_2$ is dissociated by 5.9% at 3000 K and by 96.4% at 5000 K. The oxygen atoms would recombine, if they were formed in the triplet ground state, eventually forming ozone as a short-lived intermediate. Ozone could not be detected as a product which escapes the hot spots. In fact, one calculates from the thermodynamical data involved[14] that the equilibrium $O_3 \rightleftharpoons O_2 + O$ is strongly shifted to the right-hand side at temperatures of a few 1000 K, which explains why ozone dissolved in water is decomposed under ultrasonic irradiation. The oxygen atoms could contribute to the formation of $H_2O_2$ only if they were formed in the excited singlet state: $O(^1D) + H_2O \rightarrow H_2O_2$. A contribution of 23% to the hydrogen peroxide formation by singlet oxygen atoms has been postulated by Anbar and Pecht,[15] who used an $^{18}O$ isotope labeling techniques.

*$H_2O_2$ Yield under Argon–Oxygen Mixtures.* The drastic increase in the yield of various sonolytic products upon the addition of oxygen or other reactive gases to the argon atmosphere, under which the irradiation of an aqueous solution takes place, has been observed earlier.[11,13] If the added gas is diatomic or triatomic, the yield passes through a maximum at a certain concentration of the added gas. The explanation for this phenomenon is simple: At the lower concentrations of added gas, more and more radicals from the sonolysis of water react with the added gas to form products. However, when the polyatomic gas is added to argon, the gas mixture acquires a lower value of $\gamma$ (ratio of the specific heats), and as a consequence, the temperature reached in the adiabatic compression phase of the gas bubbles is lowered. This lower temperature decreases the chemical yields at the higher concentrations of the added gas.

The yield of hydrogen peroxide is about 4 times greater under an argon (70%)–oxygen (30%) mixture than under the pure gases. The increase in yield as compared to the yield under pure argon is explained by the additional process of $H_2O_2$ formation in the presence of oxygen (eq 6) and, as compared to the yield under oxygen, by the greater yield of H + OH radical formation in the presence of 70% argon in the gas bubbles.

*Oxidation of Iodide under Argon.* The fact that appreciable amounts of $I_2$ are liberated in the sonolysis of KI solutions under argon is quite remarkable as almost no iodine is formed in the $\gamma$-irradiation of neutral iodide solutions in the 0.1 M range. In the $\gamma$-irradiation, both the oxidation of $I^-$ and the reduction of the $I_2$ formed are fast processes, the result being a small stationary concentration of $I_2$:

$$\dot{O}H + I^- \rightarrow OH^- + {}^1/_2I_2 \tag{10}$$

$$\dot{H} + {}^1/_2I_2 \rightarrow I^- + H^+ \tag{11}$$

Even in the presence of oxygen, little $I_2$ is produced by $\gamma$-rays as the $HO_2$ radical (which does not oxidize $I^-$)[16] also reduces $I_2$. The efficient formation of $I_2$ in the sonolysis of iodide solutions must be explained by a mechanism, in which reaction 10 occurs more readily than reaction 11. It should also be remembered that the yield of $H_2$ is not influenced by dissolved iodide and that OH radicals not scavenged by iodide form $H_2O_2$ (Figure 2).

These effects would be understandable, if reaction 3 (and probably reaction 2 to a lesser degree) were faster than reaction 4 in the gas bubbles. Under these circumstances, a large fraction of the H atoms would react to form $H_2$ in the gaseous phase before reaching the interface. Consequently, more OH radicals would reach the interface and form $H_2O_2$ in this region or react with iodide. This picture agrees with our previous observations and conclusions on the inhibition of the $H_2O_2$ formation by OH scavengers[9] (see Introduction).

The results of Figure 4 indicate that the efficiency of $I^-$ as a scavenger for O atoms must be as good as for OH radicals. If O atoms reacted more slowly with iodide, the curves for the solutions containing oxygen should fall more slowly with decreasing iodide concentration than that for argon. The reaction between $I^-$ and OH is known to be diffusion controlled.[17]

*Oxidation of Iodide in the Presence of Oxygen.* More iodine is liberated in the presence of oxygen than under argon, the greatest yield being observed at a concentration of 30% $O_2$ in the gas mixture (Figures 1 and 3). In the case of high iodide concentration (Figure 3) the yield of iodine is substantially greater than that of $H_2O_2$ in the absence of iodide. For example, at 30% $O_2$ the rate of $H_2O_2$ formation is $0.93 \times 10^{-4}$ M min$^{-1}$ and that of $I_2$ $1.58 \times 10^{-4}$ M min$^{-1}$; i.e., the latter rate is 1.7 times larger. At an $I^-$ concentration of 1 M, 68% of the radicals are scavenged (see Figure 2). Iodine forms with 1.7/0.68 = 2.5 times greater efficiency than $H_2O_2$ by the intermediates of the sonolysis. One of the intermediates, i.e. $HO_2$, does not even react with $I^-$ but also produces $H_2O_2$ in the presence of iodide.[16] These considerations show that the large yield of $I_2$ in the presence of oxygen cannot be accounted for unless one postulates an additional intermediate which oxidizes $I^-$ but does not contribute to the formation of $H_2O_2$. This species may be the oxygen atom in its triplet ground state:

$$O + 2I \xrightarrow{2H^+} I_2 + H_2O \tag{12}$$

It is clear from the above arguments on the $I_2$ and $H_2O_2$ yields that comparable amounts of water and oxygen molecules are dissociated upon the action of ultrasound on oxygenated water (eq 1 and 9).

*Oxidation of Formate.* In the irradiation of sodium formate solutions under argon, the hydrogen yield is the same as in the absence of formate (Figure 5). This indicates that not many of the H atoms formed in the sonolysis of water escape the hot spots to react with the formate ions: $H + HCO_2^- \rightarrow H_2 + CO_2^-$. This result agrees with Anbar and Pecht's experiments.[18] They found very little HD when they irradiated solutions of $DCOO^-$. We explain the formation of oxalic acid by the following reactions initiated by the OH radicals:

$$\dot{O}H + HCO_2^- \rightarrow H_2O + CO_2^- \tag{13}$$

$$2\dot{C}O_2^- \rightarrow (CO_2^-)_2 \tag{14}$$

The $CO_2^-$ radical is known to dimerize in neutral and alkaline solutions.[19] The yield of oxalic acid decreases with decreasing formate concentration in a fashion similar to the iodine yield from $I^-$ solutions (Figure 4). We thus arrive at a similar picture as in the discussion of the oxidation of iodide: The hydrogen atoms mainly form hydrogen in the gas bubbles while the OH radicals are more or less scavenged by the solute.

The hydrogen peroxide yield decreases with increasing formate concentration as more and more OH radicals are scavenged. However, the decrease in $H_2O_2$ yield is more pronounced than the increase in the $(CO_2^-)_2$ yield. Further, appreciable amounts of $CO_2$ are produced (Figure 5). In the presence of $H_2O_2$ and in the absence of $O_2$ the oxidation of formate is a chain reaction as $CO_2^-$ reacts with $H_2O_2$, to form $CO_2$ and to regenerate an OH

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(14) Wulf, O. R.; Tolman, R. C. *J. Am. Chem. Soc.* **1927**, *49*, 1650.

(15) Anbar, M.; Pecht, I. *J. Phys. Chem.* **1964**, *68*, 352. The observation of $H^{16}O^{18}OH$ formed in the irradiation of water under an atmosphere of $O_2$ does not prove the formation of singlet oxygen but can also be explained by the reaction $H + O_2 \rightarrow {}^{18}OH + {}^{18}O$, followed by ${}^{18}OH + {}^{16}OH \rightarrow H^{18}O^{16}OH$.

(16) Pulse radiolysis experiments to detect the reaction of $HO_2$ with $I^-$ were carried out in this laboratory by Dr. M. Bansal. An aerated solution of pH 2 containing KI at $10^{-4}$ M and formate at $5 \times 10^{-2}$ M was pulsed, and the changes in optical absorption and conductivity were followed. It is known from radiation chemistry that $HO_2$ radicals are formed in such a solution with a $G$ value of 6 radicals/100 eV. No changes could be detected up to 10 s after the pulse. It has to be concluded either that $HO_2$ is unreactive toward $I^-$ or that it reacts very slowly ($k < 10^2$ M$^{-1}$ s$^{-1}$).

(17) Farhataziz; Ross, A. B. *Natl. Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*) **1977**, *NSRDS-NBS 59*.

(18) Anbar, M.; Pecht, I. *J. Phys. Chem.* **1964**, *68*, 1460.

(19) Oxalic acid as a product of the radiolysis of formate at higher pHs has been postulated as no $CO_2$ is found,[20] but it has not yet been detected experimentally. We find that $\gamma$-irradiation of neutral or alkaline solutions under an atmosphere of $N_2O$ yields oxalate with 3 molecules/100 eV. It is known that $CO_2^-$ radicals are formed in such a solution with $G$ = 6 radicals/100 eV. No $CO_2$ was detected under these conditions. It is concluded that $CO_2^-$ radicals react in alkaline solution exclusively via dimerization.

(20) Fricke, H.; Hart, E. J. *J. Chem. Phys.* **1934**, *2*, 824.

radical which, in turn, reacts with formate to produce $CO_2^-$:[21]

$$\dot{C}O_2^- + H_2O_2 \rightarrow CO_2 + OH^- + \dot{O}H \tag{15}$$

The ratio of the yields of $CO_2$ and $(CO_2^-)_2$ is a measure of the chain length. As expected, this ratio becomes greater with decreasing oxalate yield. However, a quantitative treatment of this chain reaction is difficult to carry out as the concentration of $H_2O_2$ formed changes with the formate concentration and as $H_2O_2$ also acts as a chain-terminating reagent. It should, however, be mentioned that no oxalic acid was found when $10^{-3}$ M $Cu^{2+}$ ions were present during irradiation. $Cu^{2+}$ is known to react with $CO_2^-$ radicals to form $CO_2$.[22] This finding may be taken as an indication for the $CO_2^-$ radicals escaping the hot spots into the bulk solution where they can react with $Cu^{2+}$ in low concentration.

In the presence of oxygen (Figure 6) no chain reaction occurs as the $CO_2^-$ radicals are scavenged by $O_2$:[21,23]

$$\dot{C}O_2^- + O_2 \rightarrow CO_2 + \dot{O}_2^- \tag{16}$$

The formation of $O_2^-$ could be detected in the experiments with solutions of pH 14. Under these conditions, $O_2^-$ is known to be long-lived.[17] Reaction 16 explains why the yield of $O_2^-$ was greater in the presence of formate in the strongly alkaline solution, as part of the OH radicals were scavenged and also produced $O_2^-$. In less alkaline solutions the $O_2^-$ radicals produce $H_2O_2$ during the irradiation:

$$O_2^- \xrightarrow{H^+} {}^1/_2H_2O_2 + {}^1/_2O_2 \tag{17}$$

This explains why the yield of hydrogen peroxide is not decreased in the presence of formate. The $HO_2$ radicals do not react with formate but produce $H_2O_2$ as in the absence of this solute. An appreciable $CO_2$ yield of $0.6 \times 10^{-5}$ M min$^{-1}$ is observed even at formate concentrations as low as $10^{-3}$ M. This means that $0.6 \times 10^{-5} \times 100/(0.6 \times 10^{-5} + 2 \times 2.5 \times 10^{-5}) = 10\%$ of the radicals produced must have escaped the hot spots to react with formate at $10^{-3}$ M ($2.5 \times 10^{-5}$ M min$^{-1}$ being the yield of $H_2O_2$ in the presence of $O_2$). In the presence of oxygen, the O atoms generated in the gas bubbles may also react with formate. However, their reaction is expected to parallel that of $O_3$ and to produce $CO_2$ without forming $H_2O_2$ at the same time:

$$O + HCO_2^- \rightarrow CO_2 + OH^- \tag{18}$$

In fact, a $CO_2$ yield exceeding that of $H_2O_2$ was observed at higher formate concentrations (Figure 6).

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**Registry No.** $I^-$, 20461-54-5; $HCO_2^-$, 71-47-6.

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# Effect of Solvent Structure on Electron Reactivity: 1-Propanol/Water Mixtures

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There are pronounced effects of the solvent structure on the reaction rate constants of solvated electrons ($e_s^-$) in 1-propanol/water mixed solvents. The changes of solvent structure are also reflected in physical properties such as viscosity $\eta$ and heat of mixing, and in shifts of the optical absorption energies $E_{\epsilon_{max}}$ of $e_s^-$. The reaction rate of $e_s^-$ with nitrobenzene is nearly diffusion controlled. Variation of the rate constant $k_2$(nitrobenzene) with mol % water indicates four structural zones: (a) 0 to ~15 mol % water, the water enhances the hydrogen-bonded structure of the alcohol liquid and stiffens it, $k_2$ decreases; (b) ~15 to 75 mol % water, $\eta$ continues to increase but $k_2$(nitrobenzene) *increases*, contrary to the expected Stokes–Smoluchowsky relationship; (c) ~75 to 99% water, $\eta$ decreases and $k_2$ increases in the Stokes–Smoluchowsky manner (zone c begins at the viscosity maximum); (d) ~99 to 100% water, $\eta$ and $k_2$(nitrobenzene) decrease contrary to Stokes–Smoluchowsky. Considering the reverse direction, adding alcohol to water, the solvent structure that varies smoothly through zone c is water dominated, is somewhat different from that of pure water, and is seeded by the first 1% of 1-propanol. Values of $k_2$ for the inefficient scavengers phenol and toluene are also influenced by the binding energy of the electron in its solvation potential well.

## Introduction

The complex dependence of the physical properties of water/alcohol solutions upon composition[1] makes them valuable solvents in which to probe the behavior of solvated electrons. Examples of the physical properties are the following: (1) excess enthalpy of mixing, which is always negative in the water-rich zone, but in the alcohol-rich zone is negative for methyl and ethyl, and positive for larger alkyl groups;[1-3] (2) viscosity, where a maximum always occurs at 70–80 mol % water;[4] (3) mutual diffusion coefficients, which have a minimum at 70–80 mol % water;[5] (4) dielectric relaxation, where the relaxation time of alcohols increases with addition of a small amount of water and the relaxation time of water increases with addition of a small amount of alcohol;[6-9] (5) acoustics, where absorption in excess of the ideal values occurs due to bulk (compression/expansion) viscosity.[10,11]

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