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Conductivity of Irradiated Pure Water

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The conductivity of water having parts per billion concentrations of oxygen, hydrogen, and bicarbonate was measured while the water was irradiated by a low-pressure mercury vapor lamp, which was turned on and off periodically. A cell normally used for measurement of dissolved oxidizable carbon was modified for use in these measurements. When the lamp is turned on, the conductivity increases (sometimes decreases) with a time constant of about 50 ms; when the lamp is turned off, the conductivity changes in the opposite direction with a time constant of about 275 ms, but does not return to its value before the lamp is turned on. The lamp step (difference between conductivity with lamp on and conductivity with lamp off) depends on the intensity of radiation and on the concentrations of oxygen, hydrogen, and bicarbonate. It is negative when $[O_2]$ is less than $\approx 10^{-10}$ M and positive for higher $[O_2]$, increasing to a maximum at $[O_2] \approx 10^{-7}$ M. The presence of dissolved H_2 increases the lamp step. The lamp step increases in magnitude when the lamp intensity increases, without being proportional to intensity. Experiments were performed that show that the reactions responsible for the changes in conductivity occur in bulk solution and not at the cell electrodes. A theoretical model to explain the changes in conductivity was developed. It assumes that the absorption of a photon of ultraviolet radiation converts one molecule of water to a hydrogen and a hydroxyl radical ($H^\bullet$ and $^\bullet OH$), and that these react with H^+, OH^-, and other dissolved species. Some thirty bimolecular reactions are considered, with rate constants taken from the literature. The differential equations giving the changes in the concentrations of twelve species are solved numerically. The rate of generation of $H^\bullet$ and $^\bullet OH$ is varied with time to represent the turning on and off of the ultraviolet lamp. From the species concentrations, the conductivity is calculated as a function of time, yielding calculated lamp steps in general agreement with our experimental results. The species responsible for the lamp steps can then be identified, and the important reactions elucidated. The conductivity is always dominated by the contribution of H^+. It is shown that a substantial negative lamp step, found for very low oxygen concentrations, cannot occur in completely pure water. Dissolved carbon that has been oxidized to bicarbonate must be present. Hydroxyl radicals produced by irradiation react with HCO_3^- to give the carbonate radical anion, $C^\bullet O_3^-$. Because the p*K* of the parent acid $HC^\bullet O_3$ is substantially larger than that of H_2CO_3, formation of $C^\bullet O_3^-$ leads to a decrease in $[H^+]$ and hence a decrease in conductivity. If dissolved oxygen is present, it may be converted by $H^\bullet$ to perhydroxyl radical $H^\bullet O_2$, which dissociates to H^+ and superoxide anion $^\bullet O_2^-$, raising the conductivity. Furthermore, superoxide can reduce $HC^\bullet O_3$ back to HCO_3^-, countering the conductivity-lowering effect of bicarbonate. Because superoxide is destroyed mainly by reaction with perhydroxyl radical, and the concentration of perhydroxyl is much smaller than that of superoxide, superoxide is a long-lived species. Thus the conductivity after the lamp is turned on and then off is larger than the conductivity before the sequence. If hydrogen is present in addition to oxygen, it reacts with $^\bullet OH$ to generate $^\bullet H$, which leads to the formation of more $H^\bullet O_2$. In addition, the reaction of $^\bullet OH$ with $H^\bullet O_2$, which would convert the latter back to O_2, is prevented. For both reasons, hydrogen makes the conductivity step larger, as observed. The concentration of superoxide is limited because high $[O_2^-]$ leads to high $[H^\bullet O_2]$, so the reaction of O_2^- with $H^\bullet O_2$, which destroys O_2^-, becomes important. The experimental observation that the conductivity step goes through a maximum as a function of O_2 concentration is not explained by our model, but is believed to be associated with absorption of ultraviolet radiation by superoxide, H_2O_2, or other species formed from O_2.

I. Introduction

Irradiation of water or dilute aqueous solutions produces, initially, electrons, and hydrogen and hydroxyl radicals. These species hydrate and react very rapidly (within 10^{-9} sec) to yield longer-lived species, including hydrated electrons, H^+ and OH^-, and radicals, which then react with each other, with water molecules, and with solutes.[1,2] The rate constants for many of the reactions have been measured and reviewed,[3−7] as have the properties of the reactive species. The number of free radicals produced by radiation and how it depends on pH and dissolved oxygen are important considerations in radiation energy treat-

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ment of water.[8] For bactericidal and germicidal effects, ultraviolet radiation of wavelengths between 200 and 310 nm is most effective. The goal in radiation treatment is to reduce the concentration of organic contaminants from dilute solutions to low concentrations; we will here be concerned with concentrations below 1 μM.

The present widespread use of ultrapure water (impurity concentration < 1 μM) in the semiconductor and pharmaceutical industries has led to the commercial development of various ultraviolet radiation treatment methods, as well as instrumentation to control and monitor organic contamination. Hydrogen peroxide and in-line ultraviolet sterilization are commonly used to purify process streams. On-line instrumentation, such as the Anatel A1000 total organic carbon (TOC) analyzer, measures trace levels of organics on line by oxidizing them completely to CO_2 using ultraviolet light and measuring the resulting conductivity change. For these reasons, the need has arisen to theoretically investigate the photochemistry of UV-irradiated pure water.

In this report, we present experimental results on the change in conductivity of ultrapure water, with and without dissolved oxygen and/or hydrogen, induced by ultraviolet radiation. We then present a kinetic model which explains these conductivity changes in terms of species produced by the reactions of hydrogen and hydroxyl radicals. It is assumed that these radicals are formed quickly from whatever species are initially produced by the radiation.

There were a number of early studies of the change in water conductivity on irradiation or shocking.[9−13] Schmidt,[11] by analyzing the conductivity as a function of time with a pulsed radiation source, showed that X irradiation of pure water produced ions with a lifetime longer than 0.1 s. He reported that, in addition to a rapid rise in the conductivity (time constant ~1 s) when the source was turned on and a corresponding rapid decrease when the source was turned off, there was an irreversible conductivity increase continuing throughout the experiment. He suggested that the rapid increase and decrease were due to superoxide anion, $\cdot O_2^-$, from ionization of the conjugate acid HO_2, produced by reaction of protons with dissolved oxygen, and the irreversible increase was due to ionization of H_2CO_4, produced from dissolved CO_2. David and Hamann[9] measured a large increase in conductivity with pressure (produced by shock waves). They ascribed it to the increases in the water autoionization constant and in the degree of ionization of dissolved CO_2 via

$$CO_2 + 3H_2O \rightleftharpoons H_3O^+ + HCO_3^- + H_2O \rightleftharpoons 2H_3O^+ + CO_3^{2-} \quad (1)$$

Bielski and Gebicki[14] stated that "the presence of oxygen leads to ... reactions (which) have a profound effect on the products (of irradiation)," even though they have little effect on the primary processes (occurring within 10^{-10} sec), so that irradiation of oxygenated water must be discussed separately from irradiation of nonoxygenated water. They emphasized that the reducing species $\cdot H$ and e^-_{aq} react with O_2 better than with almost any other solute, producing $\cdot O_2^-$, whereas the reaction of the oxidizing species $\cdot OH$ with O_2 is not important. A later review of the radiation chemistry of water is found in Spinks and Woods.[15]

Since the conductivity is a sum of contributions of all charged species, measurement of conductivity as a function of energy and intensity of radiation is not the most informative way to probe the reactions. On the other hand, conductivity is a simple and very sensitive measurement that can be performed without introducing additional contamination. With typical levels of organic contamination in modern ultrapure water systems being as low as 1 ppb, UV oxidation followed by detection of conductivity changes has proven to be an effective way to measure trace levels of organics. Irradiation of pure water with 185 and 254 nm ultraviolet light from a low-pressure mercury vapor lamp results in the oxidation of dissolved carbon species to the +4 oxidation state, corresponding to (see eq 1) carbonic acid, bicarbonate, and carbonate, which raises the conductivity. From the measured increase in the conductivity, the concentration of dissolved carbon species is deduced. If the oxidation is allowed to go to completion, the resulting change in conductivity is found to be directly related to the TOC and largely independent of the concentration of dissolved oxygen but highly dependent on that of dissolved hydrogen.

The measurements of conductivity reported here have been performed using an oxidation cell of the kind employed for TOC measurements, but with the source of ultraviolet radiation being turned on and off and the conductivity measured as a function of time. In this report, we give some results for water containing known small concentrations of dissolved oxygen and/or hydrogen. The experimental results are compared with conductivities calculated from the concentrations of ionic species, obtained by integrating the rate equations for the known chemical reactions which follow irradiation of water. Rate constants from the literature are used for these. The goal was to explain the variation of conductivity with oxygen and hydrogen concentrations and with intensity of irradiation, or, if this proved to be impossible, to determine whether processes other than the known reactions are occurring.

II. Experimental Apparatus

A small, self-contained ultrapure water loop was constructed, comprising a 3.5 L 316 stainless steel reservoir, an ultrapure gear pump, an Atlantic Ultraviolet "Minipure" UV sterilizer, an 18 in.-long 1 in. diameter mixed bed DI column, an injection port, and a collection of valves to allow either the sterilizer, the DI column, or both to be switched in or out. Two Orbisphere 3500 gas analyzers were plumbed in line to allow monitoring of H_2 and O_2 gas concentrations in the water stream to ppb levels. A titanium frit sparger was placed in the reservoir and connected to a variety of gas cylinders through valves to control gas concentrations. All plumbing was made with 316 stainless steel tubing to avoid gas permeation to and from ambient.

A simplified cross-section view of the cell used for oxidation and measurement is shown in Figure 1. It consists of an 8.5 cm^3 sample volume formed by two annular titanium electrodes, a synthetic fused silica window and a ceramic backplate, arranged so that ultraviolet radiation from the annular low-pressure mercury vapor lamp (made by Jelight) illuminates the sample between the electrodes. The intensity at the surface of the lamp was 1300 $\mu W/cm^2$ at 185 nm and 25 mW/cm^2 at 254 nm.

The cell constant for measurement of conductivity was determined to be 0.069 cm. For completely pure water, the conductance should be (section V) $5.50 \times 10^{-6}\ \Omega^{-1}\ m^{-1}$ or 55 nS. The conductance actually measured for our pure water samples before irradiation was never more than a few percent higher than 55 nS. During irradiation in the cell, the conductance increases (sometimes decreases) because of the creation of new charged species. When the irradiation source is turned off, a rapid decrease (sometimes increase) in conductivity is observed.

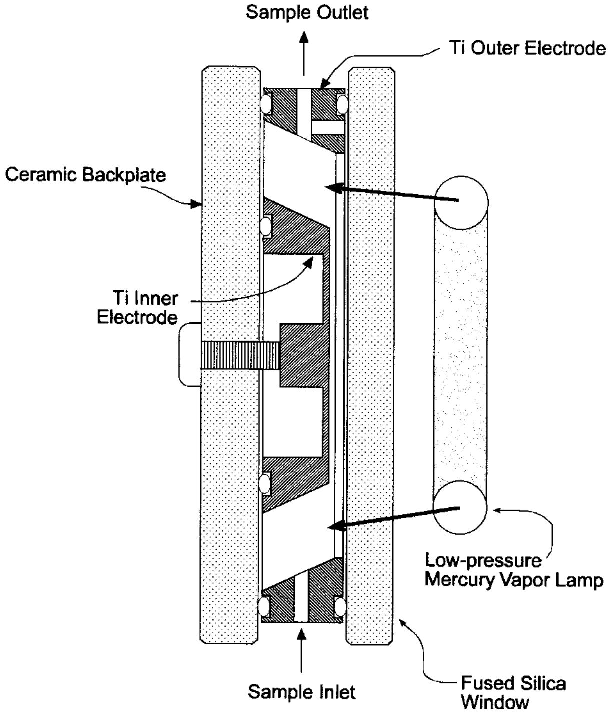

Figure 1. Cross-section of the cell used for measurement of conductivity. The mercury vapor lamp illluminates the sample of water held in the cell. Voltage and current are measured between the two titania-coated titanium electrodes. The area of water irradiated by the lamp is 14.186 cm^3, and the intensity of radiation is 1300 μW/cm^2.

III. Experimental Results

A series of experiments was performed, with a static water sample trapped in the cell, in which the ultraviolet lamp was turned on and off and conductance was measured as a function of time. An active compensating voltage was introduced to force the dc Faradaic current to be zero, and the change in the conductivity accompanying illumination or interruption of illumination was recorded. The results of Figure 2 are typical.

At 1 min, the flow valve is closed to trap the sample and at 2 min the lamp is turned on. The lamp is then turned off and on periodically until the end of the run: the lower graph in (a) shows lamp current as a function of time. The upper graph in (a) shows the water temperature during the run; it can be seen to rise about 10 °C over the 18-minute period that the lamp is on. In (b) and (c), the measured conductance as a function of time is graphed (solid curves) for two runs, showing the response of the system. The O_2 concentration is 1.2 ppb by weight in (b) and 1082 ppb by weight in (c).

In the latter case one can see that, each time the lamp is turned on, the conductivity rises quickly to a higher value, this change being referred to as a “positive lamp step.” Correspondingly, the conductivity falls quickly when the lamp is shut off. For the lower O_2 concentration, the steps are much smaller and harder to see. In both cases, the steps are superimposed on a gradual, almost linear, increase in conductivity with time, shown by the dotted lines in (b) and (c). Figure 3 shows, on a finer time scale, the rise and fall of the measured conductivity when the lamp is turned on and off once. Note that the time constant for the rise is smaller than the time constant for the fall; they are estimated to be about 50 ms and about 275 ms, respectively.

Figure 4 shows results for a run similar to that of Figure 2(c), but with the O_2 level reduced to 18 ppb. On close inspection, the conductivity can be seen to go slightly *lower* each time the lamp is turned on (with the exception of the first time) and slightly *higher* each time the lamp is turned off. This reverse step we refer to as a “negative lamp step.”

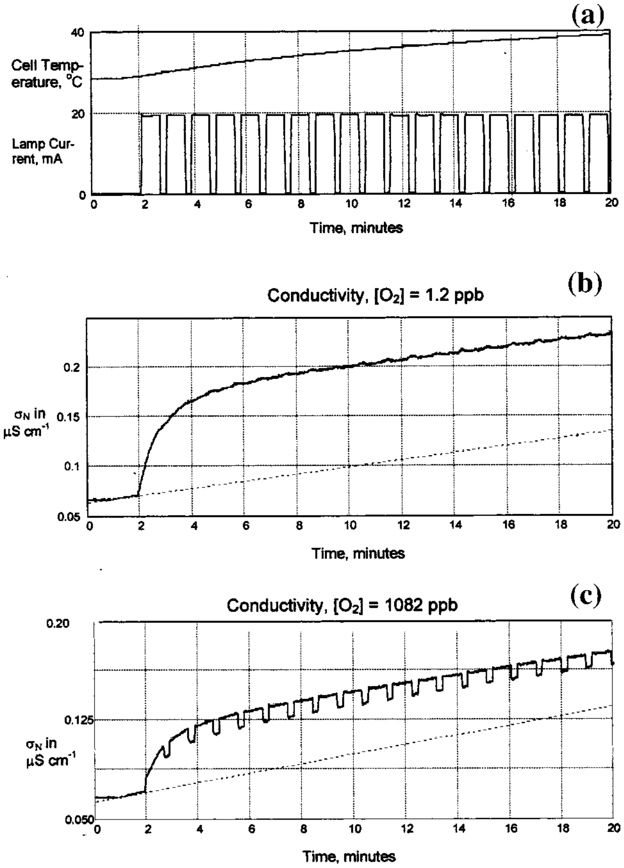

Figure 2. Experimental results for two water samples. The lamp was turned on at $t = 2$ min, held at constant intensity for almost 1 min, held off for a short time, and the cycle repeated, as shown in the lower plot of (a). The upper plot of (a) shows the temperature in the cell as a function of time. Plots (b) and (c) show conductivity as a function of time for two samples, with oxygen concentrations of 1.2 and 1082 ppb. In (c), the conductivity is seen to increase each time the lamp is turned on and to decrease each time it is turned off.

The gradual rise in the measured conductivity, on which the steps are superimposed, is associated with the increase in the temperature of the water as the lamp warms the oxidation chamber. At ppb levels of TOC, the temperature coefficient of conductivity for water is about +3.5 nS/°C, so that this accounts for most of the underlying conductivity slopes, which are shown as dotted lines in Figures 2(b), 2(c), and 4(c). In using conductivity to measure TOC, one uses the temperature-compensated difference in conductivity at the end of oxidation.

The height of the rising step, defined as current with lamp on minus current with lamp off, depends on the intensity of illumination, as well as on the concentrations of bicarbonate, dissolved hydrogen, and oxygen, but is roughly independent of the TOC concentration. The step height is observed to increase with the lamp intensity without being proportional to it. It also depends markedly on the concentrations of dissolved H_2 and dissolved O_2. Figure 5 shows the step in conductance as a function of the concentration of dissolved O_2. Although the step is usually positive, increasing with $[O_2]$, it becomes negative for $[O_2]$ less than about 10^{-4} μM and reaches a maximum for $[O_2]$ about 0.1 μM, dropping off thereafter.

Explaining the conductance steps, and how they depend on lamp intensity and concentrations of dissolved H_2 and dissolved O_2 will be our primary concern here. The effect of irradiation on dissolved carbon will not be considered quantitatively in this

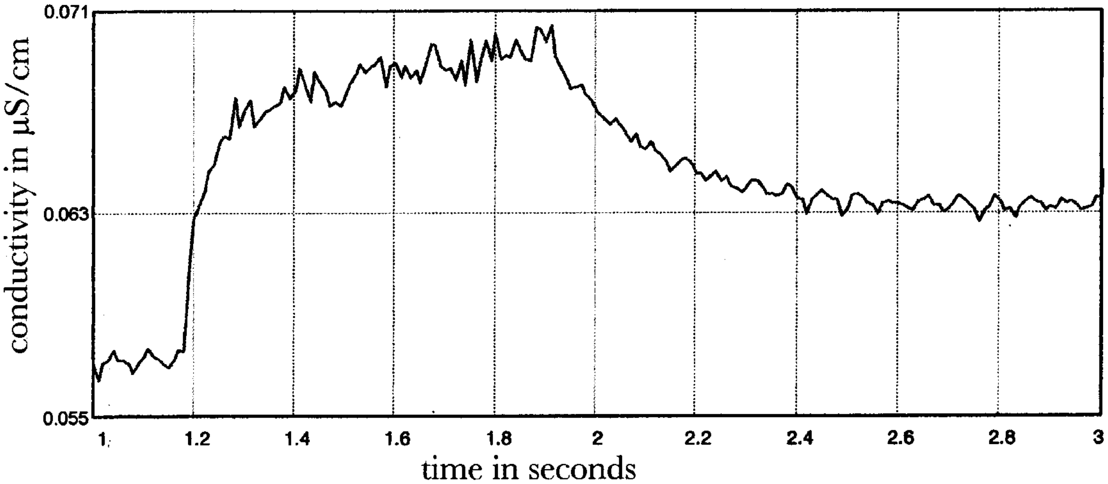

Figure 3. Details of rise and fall of conductivity when lamp is turned on (at 1.1 s) and off (at 1.9 s). The rise in conductivity when the lamp is turned on is much faster than the fall when the lamp is turned off.

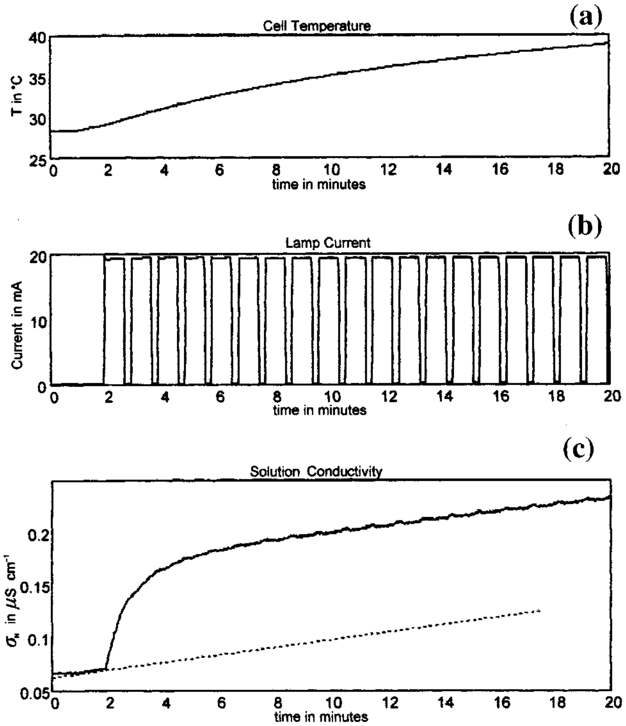

Figure 4. Experimental results for irradiation of water containing 18 ppb O_2. The lamp is turned on and off according to (b). Plot (a) shows cell temperature as a function of time and plot (c) shows solution conductivity as a function of time. In this case, the conductivity (after the initial rise) falls when the lamp is turned on and increases when it is turned off.

study. It should be noted, however, that a number of experiments have been performed that indicate that the oxidation of dissolved carbon takes place in bulk solution, and not at the electrodes.

For example, a series of experiments was performed in which the geometry of the cell and the ultraviolet source was changed to vary the irradiated area of the electrodes. The rate of oxidation of carbon to bicarbonate was measured and observed to be proportional to the exposed surface area of the solution, rather than to the electrode area that was irradiated. In other experiments, the Faradaic current, which should correspond to oxidation and reduction at the electrodes, was actively eliminated using servo feedback, and there was no change in the apparent oxidation rate (rate of conductivity increase).

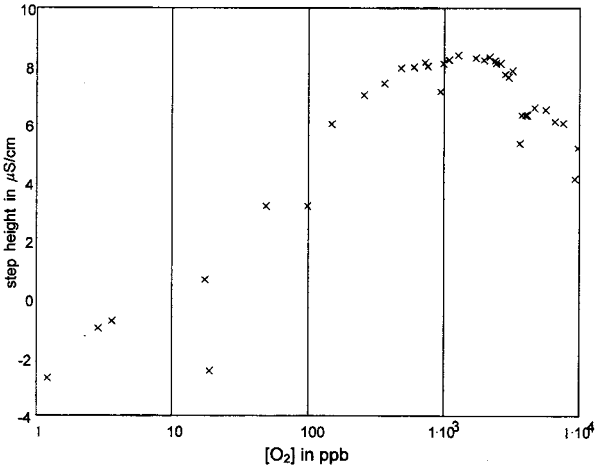

Figure 5. Measured conductance step as a function of oxygen concentration. The step height is negative for $[O_2]$ less than about 10 ppb and positive for higher concentrations. It apparently goes through a maximum value for $[O_2]$ near about 10^3 ppb.

Irradiation changes the oxidation number of dissolved carbon from −2, if the carbon is assumed to be in the form of methanol, to +4, corresponding to bicarbonate. Probably, a number of reactions with radiation-generated species occur, in each of which the oxidation number changes by unity.[16] A possible sequence of species is methanol → methanol radical $\cdot CH_2OH$ → formaldehyde → the radical $\cdot CHO$ → formic acid or formate → formate radical $\cdot CO_2H$ → bicarbonate or carbonic acid. Each step may result from a hydroxyl radical removing a hydrogen radical, forming water and raising the oxidation number by 1. This will be discussed in the future.

IV. Methods of Calculation

The specific conductivity κ is given by a sum of contributions of all the ionic species present:

$$\kappa - \sum_i \rho_i \lambda_i \tag{2}$$

where ρ_i is the (molar) concentration of species i and λ_i is the molar ionic conductivity of this species. In our calculations, tabulated values are used for molar ionic conductivities of all species for which they are known. Species of unknown molar ionic conductivity are given the value of 45 S cm^{-1} M^{-1}. The species concentrations ρ_i are calculated by integrating the kinetic equations that describe the radiation-induced dissociation of H_2O to H and OH radicals and the reactions of these radicals with each other and with other species present.

The rate of the initial reaction, the decomposition of water to form •H and •OH radicals, is proportional to the radiation intensity. The intensity of radiation, typically $I_o = 1300\ \mu$watts/cm^2 as it enters the cell, decreases with depth z according to

$$I = I_o \exp[-\epsilon_w z]$$

where the absorption coefficient of water, ϵ_w, is about 1.8 cm^{-1}. Thus, essentially all the radiation is absorbed by the sample if its thickness c is more than a few cm. Because the intensity varies with z, concentrations of the solution species that contribute to the conductivity will vary with z. The voltage across the electrodes ΔV being fixed, the current density will depend on depth

$$j(z) = \kappa(z)\Delta V$$

The average current density is $(1/c)\int_0^c j(z)\,dz$, so that the apparent conductivity is the average, $(1/c)\int_0^c \kappa(z)\,dz$ (one here has conductors in parallel). In the present article, we calculate the average conductivity only, corresponding to the average illumination intensity.

When high-energy radiation is absorbed by water, electrons are emitted, forming H_3O^+, which dissociates to hydrated protons and hydroxyl radicals •OH.[17] Within 10^{-12} sec hydrated electrons e^-_{aq} are formed, having[18] a molar conductance close to that of hydroxide ion.[19] The hydrated electrons themselves disappear in less than 50 μs, usually by reaction with H^+ to give •H.[18,19] Photons of wavelength 185 nm have an energy of 1.074×10^{-18} J or 6.70 eV, much less than the ionization potential of $H_2O(g)$, 12.62 eV,[20] so that they are not capable of ionizing H_2O, as stated by Halliwell and Gutteridge.[21] However, Spinks and Woods[15] suggest that the threshold energy for electron formation in liquid may be as small as half its value in vapor, in which case formation of e^-_{aq} would be possible. The hydrated electrons would react rapidly with H_2O to give •H and OH^-, or with H_3O^+ to give H_2O and •H;[22] the half-life of e^-_{aq} at pH 7 is less than 2.1×10^{-4} sec.[23] We have done some calculations assuming hydrated electrons are produced and react with other aqueous species. The results, not given here, are very close to those from the model we use, which assumes that only •H and •OH are produced initially, showing that it is not necessary to consider e^-_{aq}.

The average bond energy of H_2O is 4.76 eV[24] and $\Delta H°$ for $H_2O(g) \rightarrow {\cdot}H(g) + {\cdot}OH(g)$ is 5.17 eV per molecule,[24] well within the photon energy. We assume therefore that the photons dissociate water to •H and •OH. We write the initial reaction as first order

$$H_2O \rightarrow H{\cdot} + {\cdot}OH \tag{3}$$

with $d[H{\cdot}]/dt = d[{\cdot}OH]/dt = k_0[H_2O]$, and $[H_2O] = 55.5$ M. The value of k_0 is obtained as follows: The lamp intensity at the top of the cell ($z = 0$) is typically $I_o = 1300\ \mu$W/cm^2. Since the cross-sectional area is 14.186 cm^2, 1.718×10^{16} photons enter the cell per second. The intensity as a function of depth z is given by $I = I_o\, e^{-kz}$ with $k = 1.8$ cm^{-1} the absorption coefficient, so the energy absorbed per unit volume per unit time is kI, and the number of photons absorbed per unit volume per unit time is $kI/(h\nu)$. Multiplying by a factor f ($f < 1$) to take into account quantum yield and attenuation, the rate of dissociation of H_2O to H• and •OH per unit volume is $f(1.8\ \text{cm}^{-1})\, I/(1.074 \times 10^{-18}\text{J})$. Dividing by $[H_2O] = 55.5$ M and Avogadro's number, this gives a rate constant of

$$k_0 = 5.01 \times 10^{-5} f\, \{I/(W/cm^2)\} M\ sec^{-1}$$

For an intensity of 1.3×10^{-3} W/cm^2, this gives a rate of $3.62 \times 10^{-6} f$ M sec^{-1}.

The reactions we consider first in our model are shown in Table 1. The numbering of the reactions is arbitrary. Most of the values of the rate constants for these reactions are taken from the review article by Buxton et al.[4] or from the earlier reports by Ross and collaborators.[3] Exceptions to this are noted in footnotes in the table.

The reaction of the hydrogen radical •H with OH^- to produce e^-_{aq} (hydrated electron) and water is not considered. It has a rate constant of 2.3×10^7 M^{-1} sec^{-1}, which is not smaller than some of those in Table 1. This reaction, in alkaline solution, may compete with other reactions of •H[23,25] but, as will be seen, our solutions are always acidic, so that we do not consider this path to e^-_{aq}. Swallow[26] has stated that there is no practical method to convert •OH to e^-_{aq}. Consequently, we ignore all reactions involving e^-_{aq} as a reactant.

The hydroxyl radical •OH is the main oxidizing radical formed by irradiation.[27] A strong oxidant, it converts H_2O_2 to $\cdot HO_2$ (although in the presence of dissolved oxygen this is not a very important route to $\cdot HO_2$). Reactions and properties of •OH are given in Table 7.10 of Spinks and Woods,[15] and its reactions with organic species are tabulated on p 291 of ref 26. The hydroxyl radical oxidizes species such as aminoalkenes, benzene, and methanol.[2,26] It reacts with hydrocarbons to give H_2O and hydrocarbon radicals, with the latter adding O_2 to give $\cdot RO_2$ radicals. It also abstracts H from alcohols, preferably from α C−H bonds, but sometimes from other C−H or O−H bonds. The α radicals formed, R•CHOH, are reducing agents, forming $RCHOH^+$, which dissociates to RCH═O and H^+.[26] These reactions lead to the complete mineralization of organics to CO_2, which represents the highest oxidation level of carbon (IV).

The H atom also reacts with organic species, with rate constants[28] of size $\sim 10^{10}$, but, being a reducing agent, H• neutralizes •OH radicals and often replaces hydrogen atoms abstracted from organic molecules. For this reason, hydrogen must be removed from the system to effect complete mineralization. This is effectively done by O_2 which acts as an efficient hydrogen atom scavenger. Sometimes, H• acts as an oxidizing agent, removing H• from organic molecules and forming H_2.[29,30]

Although •OH can act as an acid to release H^+ and $\cdot O^-$, its high pK (11.9) means that $[\cdot O^-]$ is appreciable only in basic solutions.[22] Therefore, we do not consider reactions of $\cdot O^-$ in our model. If the ionization reaction of •OH is considered to go to equilibrium, $[\cdot O^-]$ can be calculated from [•OH] and the pH. Spinks and Woods[27] give a rate constant of 3×10^9 M^{-1} sec^{-1} for the reaction of •OH with O_2 to give $H^+ + O_3^-$, but this is absent from Buxton et al.'s compilation;[4] presumably O_3^- is formed by reaction of $\cdot O^-$, formed from •OH, with O_2.

V. Calculation of Conductivity Decrease

We first consider the decrease in conductivity caused by irradiation of water in the absence of dissolved oxygen. It is easy to show that irradiation of completely pure water cannot lead to a substantial decrease in conductivity. To begin with, the only ionic species present are H^+ and OH^-, in equal concentrations. From $K_w = 1.0075 \times 10^{-14}$, $[H^+] = [OH^-] =$

TABLE 1: Reactions Considered in Our Model and Rate Constants[a]

number	reaction	rate constant	ref.
1	$H\cdot + H\cdot \rightarrow H_2$	$k_1 = 4.5 \times 10^9\ M^{-1}\ s^{-1}$	e
2	$H\cdot + H_2O \rightarrow H_2 + \cdot OH$	$k_2 = 10\ M^{-1}\ s^{-1}$	
3	$H\cdot + \cdot OH \rightarrow H_2O$	$k_3 = 1.5 \times 10^{10}\ M^{-1}\ s^{-1}$	d
4	$H\cdot + O_2 \rightarrow HO_2\cdot$	$k_4 = 2.1 \times 10^{10}\ M^{-1}s^{-1}$	
5	$H\cdot + H_2O_2 \rightarrow \cdot OH + H_2O$	$k_5 = 3.5 \times 10^7\ M^{-1}\ s^{-1}$	f
7	$\cdot OH + \cdot OH \rightarrow H_2O_2$	$2k_7 = 1.1 \times 10^{10}\ M^{-1}s^{-1}$	
8	$\cdot OH + O^- \rightarrow \cdot HO_2$-	$k_8 = 1 \times 10^{10}\ M^{-1}\ s^{-1}$	
9	$\cdot OH + OH^- \rightarrow H_2O + O^-$	$k_9 = 1.3 \times 10^{10}\ M^{-1}\ s^{-1}$	
10	$\cdot OH + H_2O_2 \rightarrow H_2O + H\cdot O_2$	$k_{10} = 2.7 \times 10^7\ M^{-1}s^{-1}$	
12	$\cdot OH + H\cdot O_2 \rightarrow H_2O + O_2$	$k_{12} = 2.8 \times 10^{10}\ M^{-1}\ s^{-1}$	c
13	$\cdot OH + \cdot O_2^- \rightarrow OH^- + O_2$	$k_{13} = 9.0 \times 10^9\ M^{-1}\ s^{-1}$	e
14	$\cdot O^- + H_2O \rightarrow OH^- + \cdot OH$	$k_{14} = 1.8 \times 10^6\ M^{-1}\ s^{-1}$	
20	$H^+ + OH^- \rightarrow H_2O$	$k_{20} = 1.3 \times 10^{11}\ M^{-1}\ s^{-1}$	
21	$H_2O \rightarrow H^+ + OH^-$	$k_{21} = 2.36 \times 10^{-5}\ s^{-1}$	
22	$\cdot OH + H_2 \rightarrow H\cdot + H_2O$	$k_{22} = 3.5 \times 10^8\ M^{-1}\ s^{-1}$	e
29	$HCO_3^- + \cdot OH \rightarrow \cdot CO_3^- + H_2O$	$k_{29} = 8.5 \times 10^6\ M^{-1}\ s^{-1}$	
30	$H\cdot + \cdot CO_3^- \rightarrow HCO_3^-$	$k_{30} = 5.7 \times 10^{10}\ M^{-1}\ s^{-1}$	
33	$\cdot CO_3^- + \cdot CO_3^- \rightarrow$ products	$k_{33} = 1 \times 10^7\ M^{-1}\ s^{-1}$	
34	$H\cdot O_2 + O_2^- (+ H_2O) \rightarrow O_2 + H_2O_2 + OH^-$	$k_{34} = 9.6 \times 10^7\ M^{-1}\ s^{-1}$	b
35	$O_2\cdot + \cdot CO_3^- + H_2O \rightarrow HCO_3^- + OH^- + O_2$	$k_{35} = 4 \times 10^8\ M^{-1}\ s^{-1}$	

[a] Rate constants from Buxton et al.[4] except where indicated in ref. column. [b] Christensen, H.; Sehested, K. *J. Phys. Chem.* **1988**, *92*, 3007−3011. [c] Elliot, A. J.; Buxton, G. V. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 2465−2470. [d] Buxton, G. V.; Elliot, A. J. *J. Chem. Soc., Faraday. Trans.* **1993**, *89*, 485−488. [e] Elliot, A. J.; Ouellette, D. C. *J. Chem. Soc., Faraday. Trans.* **1994**, *90*, 837−841. [f] Mezyk, S. P.; Bartels, D. M. *J. Chem. Soc., Faraday. Trans.* **1995**, *91*, 3127−3132.

1.004×10^{-7}M, so that, in the absence of irradiation,

$$\kappa = 1.004 \times 10^{-7}(349.8 + 198.0)\ L^{-1}\ cm^2\ \Omega^{-1} = 5.50 \times 10^{-8}\ \Omega^{-1}\ cm^{-1}$$

Suppose that the irradiation leads to the formation of a positive ion X^+ at concentration c. Then one must have $[OH^-] = [H^+] + c$ and $[H^+][OH^-] = K_w$, so that

$$[H^+] = \frac{1}{2}(-c + \sqrt{c^2 + 4K_w})$$

and the conductivity in $L^{-1}\ cm^2\ \Omega^{1-}$ becomes

$$\kappa = (\lambda_X - 76)c + 274\sqrt{c^2 + 4K_w}$$

where λ_X is the equivalent conductivity of X^+.

The value of c giving the minimum conductivity is found by setting $d\kappa/dc = 0$ and gives

$$\kappa = \sqrt{c4K_w[274^2 - (\lambda_X - 76)^2} \tag{4}$$

Even if $\lambda_X = 0$, κ is reduced only to $5.28 \times 10^{-8}\ \Omega^{1-}\ cm^{-1}$. For higher values of c than that giving the minimum, the conductivity increases because the hydroxide ion concentration increases more rapidly than the hydrogen ion concentration decreases. The calculation is similar if one assumes that a negative ion is created, replacing some of the hydroxide ion. Only a small decrease in conductivity can be achieved before the concentration of hydrogen ion increases by more than the hydroxide concentration decreases, and there is a net increase in conductivity.

Furthermore, it is difficult to imagine an ionic species with small mobility formed by the reaction of one of the products of irradiation ($\cdot H$ and $\cdot OH$) with either H^+ or OH^-. An obvious candidate, the hydrogen molecular ion H_2^+, well-known in the gas phase, can be ruled out. Although it "may" be produced in strongly acid solutions by addition of $H^\bullet$ and H^+,[31] the rate constant for H_2^+ formation in solution is believed to be less than 10^4 M/sec.[26,32,33]

In fact, we have observed a negative lamp step only in the almost complete absence of dissolved oxygen and hydrogen, and only when the conductivity before irradiation is significantly higher than that of pure water, implying that species other than H^+ and OH^- are present. One may suppose that some of the dissolved carbon has been oxidized to the +4 state and is present as bicarbonate ion, HCO_3^-, at the parts per billion level. One part per billion corresponds to $[HCO_3^-] = 5.55 \times 10^{-8}$M. It is easy to calculate conductivity as a function of $[HCO_3^-]$ by combining electroneutrality, $[H^+] = [OH^-] + [HCO_3^-]$ and the equilibrium condition $[H^+][OH^-] = K_w$. If $[HCO_3^-] = 5.55 \times 10^{-8}$M, $[H^+] = 1.319 \times 10^{-7}$M and $[OH^-] = 7.64 \times 10^{-8}$M. Since $\lambda_{HCO3-} = 44.5\ cm^2\ \Omega^{1-}\ equiv^{-1}$, the conductivity would be $6.36 \times 10^{-8}\ \Omega^{-1}\ cm^{-1}$. For $[HCO_3^-]$ large compared to $\sqrt{K_w}$, the equations yield $[H^+] = [HCO_3^-]$ and $\kappa = 394.3\ [HCO_3^-]\ cm^2\ \Omega^{-1}\ equiv^{-1}$ or $2.19 \times 10^{-8}\ \Omega^{-1}\ cm^{-1}$ per ppb $[HCO_3^-]$.

If bicarbonate or carbonate is present, it can be oxidized to the carbonate radical ion, $\cdot CO_3^-$, by $\cdot OH$ according to reaction 29 of Table 1.[4] The reaction of $H\cdot$ with HCO_3^- is much slower, with a rate constant of $4.4 \times 10^4\ M^{-1}s^{-1}$. The conversion of HCO_3^- to $\cdot CO_3^-$ would have little direct effect on the conductivity, since the equivalent conductivities of HCO_3^- and $\cdot CO_3^-$ are probably about the same. However, the pK of $H\cdot CO_3$ is 9.6 (34), much greater than the pK of H_2CO_3 (6.357), so that conversion of HCO_3^- to $\cdot CO_3^-$ results in the formation of $H\cdot CO_3$ with a consequent decrease in $[H^+]$ and in the conductivity.

Because formation of $\cdot CO_3^-$ constitutes a route for the destruction of $\cdot OH$, our models necessarily include the oxidation of bicarbonate to carbonate radical ion (the concentrations of carbonate and carbonic acid are too small to require consideration). Thus, the following reactions are considered: dissociation of water by radiation, reaction of $\cdot OH$ with HCO_3^-, reaction of $H\cdot$ with $\cdot CO_3^-$, combination of two $\cdot CO_3^-$ to form unknown products [the most important mechanism for destruction of $\cdot CO_3^{-\ 35}$], recombination of $H\cdot$ and $\cdot OH$, reaction of $H\cdot$ with H_2O to give $H_2 + \cdot OH$, formation of H_2 from $2H\cdot$, and formation of H_2O_2 from $2\cdot OH$.

The steady-state concentrations of eight species ($H\cdot$, $-\cdot OH$, H^+, OH^-, H_2CO_3, HCO_3^-, $H\cdot CO_3$, and $\cdot CO_3^-$) are determined

TABLE 2: Steady-State Conductivities (in nS/cm) Assuming No O_2 or H_2 Present[a]

k_0 [HCO_3^-]$_0$	0.01	0.02	0.04	0.08	0.16	0.32	0.5	0.7	1
0	56.37	57.81	61.09	69.17	90.22	143.20	209.70	286.40	403.60
3.24×10^{-9}	55.19	55.32	55.60	56.19	57.56	61.18	66.60	74.01	87.14
5.90×10^{-9}	55.23	55.40	55.75	56.50	58.26	62.86	69.63	78.69	94.34
1.08×10^{-8}	55.27	55.48	55.93	56.88	59.12	64.92	73.32	84.31	102.90
1.96×10^{-8}	55.32	55.59	56.14	57.34	60.13	67.36	77.63	90.83	112.70
3.58×10^{-8}	55.38	55.70	56.38	57.86	61.30	70.15	82.52	98.14	123.60
6.51×10^{-8}	55.44	55.83	56.64	58.41	62.56	73.16	87.74	105.90	135.10

[a] k_0 values in s^{-1}; bicarbonate concentrations in μM.

by solving eight simultaneous equations, including three steady-state equations, one conservation equation, three ionization equilibria, and the equation for local electroneutrality. The steady-state equations are

$$d[H\cdot]/dt = k_0[H_2O] - k_{30}[H\cdot][\cdot CO_3^-] - k_2[H\cdot][H_2O] - k_3[H\cdot][\cdot OH] - 2k_1[H\cdot][H\cdot] = 0 \quad (5)$$

$$d[\cdot OH]/dt = k_0[H_2O] - k_{29}[\cdot OH][HCO_3^-] + k_2[H\cdot][H_2O] - k_3[H\cdot][\cdot OH] - 2k_7[\cdot OH][\cdot OH] = 0 \quad (6)$$

$$d[\cdot CO_3^-]/dt = k_{29}[\cdot OH][HCO_3^-] - k_{30}[H\cdot][\cdot CO_3^-] - 2k_{33}[\cdot CO_3^-][\cdot CO_3^-] = 0 \quad (7)$$

The conservation equation is

$$[H_2CO_3] + [HCO_3^-] + [\cdot HCO_3] + [\cdot CO_3^-] = [HCO_3^-]_0 + [H_2CO_3]_0 \quad (8)$$

where $[HCO_3^-]_0$ is the original bicarbonate concentration. The ionization equilibria are for carbonic acid,

$$\frac{[H^+][HCO^-]}{H_2CO_3} = K_a = 4.4 \times 10^{-7} \quad (9)$$

for $H\cdot CO_3$,

$$\frac{[H^+][\cdot CO_3^-]}{[H\cdot CO_3]} = K_d = 10^{-9.6} = 2.51 \times 10^{-10} \quad (10)$$

and the autoionization of water,

$$[H^+][OH^-] = K_w = 1.007 \times 10^{-14} \quad (11)$$

As mentioned, the ionization of OH to give $\cdot O^-$ is important only at very high pH.[22] The steady-state condition on $\cdot O^-$,

$$d[\cdot O^-]/dt = k_8[\cdot OH][OH^-] - k_{14}[\cdot O^-][H_2O] = 0$$

requires

$$\frac{[\cdot O^-][H_2O]}{[\cdot OH][OH^-]} = K = \frac{1.3\times 10^{10}}{1.8\times 10^{6}}$$

Since $[H_2O]$ is essentially 55.5M, $[\cdot O^-] = 130[\cdot OH][OH^-]$. The concentration of O^- is in fact negligible in every case we have considered.

Taking the specific conductance of the carbonate radical ion as 45 S cm^2 mol^{-1} (close to the value for bicarbonate), we calculate the conductance as:

$$\kappa = 349.6[H^+] + 199.1([OH^-] + [O^-]) + 44.5[HCO_3^-] + 45[\cdot CO_3^-] \quad (12)$$

Table 2 shows calculated conductances in nS cm^{-1} without and with irradiation (k_0 values given), for various starting concentrations of bicarbonate ion.

The conductivities increase with k_0 for a fixed initial bicarbonate concentration, and increase with bicarbonate concentration for a fixed k_0. However, for each $[HCO_3^-]$ the calculated conductance for $k_0 \rightarrow 0$ is lower than the conductance for $k_0 = 0$ (no irradiation). The reason for this is that the steady state for any nonzero k_0 corresponds to almost complete conversion of bicarbonate (and H_2CO_3) to carbonate radical ion (and HCO_3). (The conversion is not complete because, in the steady state, the rate of conversion of bicarbonate ion to carbonate radical ion by $\cdot OH$ is equal to the rate of conversion of the radical ion to bicarbonate by $H\cdot$.)

In a more complete model, neither steady-state nor equilibrium is assumed. Instead, the rate equations are integrated in time, with given initial concentrations of H^+, OH^-, H_2CO_3, and HCO_3^-. In addition, to the formation of $H\cdot$ and $\cdot OH$ by radiation, $H_2O \rightarrow H\cdot + \cdot OH$, we consider reactions 1, 2, 3, 7, 9, 14, 20, 21, and 22 of Table 1. In the absence of dissolved oxygen or hydrogen, the species present in irradiated solution are $H\cdot$, $\cdot OH$, H^+, OH^-, HCO_3^-, $\cdot CO_3^-$, $\cdot O^-$, H_2, and H_2O_2. Hydrogen peroxide is formed by combination of two $\cdot OH$ radicals, and only reactions 5 and 10 can destroy it, so that its concentration continues to increase. As mentioned above, we neglect the formation of hydrated electrons by reaction of $\cdot H$ and OH^- because the rate constant is only 2.2×10^7, and consequently do not include any reactions involving the hydrated electron.

The rate constant for combination of H^+ and OH^- (reaction 20) is known.[36,37] The rate constant for dissociation of H_2O to H^+ and OH^- (reaction 21) is chosen so that the equilibrium condition is

$$[H^+][OH^-] = 1.82 \times 10^{-16}[H_2O] = 1.007 \times 10^{-14}$$

Reaction 22 is not important as long as $[H_2]$ is not appreciable. However, H_2 may be formed by combination of two $H\cdot$ radicals (reaction 1), or by the reaction of $H\cdot$ with H_2O (reaction 2). Furthermore, reaction 10 makes it necessary to consider O_2 as well as H_2, since the HO_2 formed from H_2O_2 may ionize to H^+ and O_2^-, and there are a number of reactions which can convert O_2^- to O_2. Therefore, even solutions not originally containing H_2 or O_2 must be treated with the more general model discussed in the next section.

VI. Calculated Steps in the Presence of O_2 and H_2

If oxygen is present, it reacts rapidly with atomic hydrogen to produce the perhydroxyl (sometimes called hydroperoxyl) radical $HO_2\cdot$, according to

$$H\cdot + O_2 \rightarrow HO_2\cdot \qquad k_4 = 2.1 \times 10^{10} \tag{13}$$

Although the perhydroxyl radical is an unimportant primary species resulting from irradiation, it is an important secondary species in oxygenated solutions. Since the p*K* of the perhydroxyl radical is only 4.7, it ionizes readily to H^+ and the superoxide radical, $\cdot O_2^-$; this is one of the most important processes involving oxygen radicals formed by irradiation.[22] The ionization of perhydroxyl to superoxide would by itself lead to an increase in the conductivity. In addition, $\cdot O_2^-$ reduces the carbonate radical ion to form bicarbonate and molecular oxygen

$$\cdot O_2^- + \cdot CO_3^- + H_2O \rightarrow HCO_3^- + OH^- + O_2 \qquad k_{35} = 4 \times 10^8$$

which cancels some of the decrease in conductivity accompanying the conversion of bicarbonate to carbonate radical ion.

A related reaction, in which oxygen oxidizes the carbon dioxide radical $\cdot CO_2$ to CO_2^- (which may be formed by reduction of CO_2)

$$O_2 + \cdot CO_2 \rightarrow CO_2^- + O_2^{\cdot -} \qquad k = 2 \times 10^9 \text{ M sec}^{-1}$$

is a mechanism for the generation of superoxide in aqueous solutions.[22] Perhydroxyl radical, the parent acid to superoxide, is not as good a reductant as superoxide, which helps explain why the rate constant for reaction of $\cdot O_2^-$, with HO_2 ~1×10^8 M sec^{-1}, is so much larger than that for reaction of HO_2 with itself, ~9×10^5 M sec^{-1}, or that for reaction of $\cdot O_2^-$ with itself, less than 0.35 M^{-1} sec^{-1}.[22] In the reaction of $\cdot O_2^-$ with $HO_2\cdot$, the former is reducing the latter. The reaction of two perhydroxyls produces O_2 and H_2O_2, while the reaction of two superoxides produces O_2 and O_2^{2-}, the dianion of H_2O_2. Neither reaction is considered in our model because the rate constants are so low.

Other oxygen species sometimes found in solution include $\cdot O^-$, the conjugate base of $\cdot OH$, and $\cdot O_3^-$, formed by the reaction of $\cdot O^-$ with O_2. The ozonide ion $\cdot O_3^-$ can be protonated to $HO_3\cdot$, which decomposes to $\cdot OH + O_2$.[22] As we calculate below, the concentration of $\cdot O^-$ is very low except at high pH, so that we neglect all reactions involving $\cdot O^-$ and $\cdot O_3^-$ in our model.

Since oxygen is generated from water during irradiation, the steady states referred to in Section V are unattainable in our experiments. Irradiation of water containing bicarbonate, but having oxygen concentration less than 1 ppb, would lead to a decrease in conductivity only for a short time. The oxygen generated at the same time as the carbonate radical anion would, if not removed, eventually lead to an increase in conductivity.

Instead of seeking steady states, we integrate the rate equations numerically. The concentrations of twelve species are followed as a function of time: $H\cdot$, $\cdot OH$, H^+, OH^-, O_2, $O_2^{\cdot -}$, HO_2, H_2O_2, HCO_3^-, H_2CO_3, $\cdot CO_3^-$, and $H\cdot CO_3$. From these we calculate the conductivity. The reactions considered, in addition to those used previously (1, 2, 3, 7, 29, and 30 of Table 1) are reactions 4, 5, 6, 10, 12, 13, 22, 29, 34, and 35 of Table 1 and all those in Table 3. Reaction 34 is the most important mechanism for the destruction of superoxide, not its reaction with itself.[38,39]

The perhydroxyl radical HO_2 can protonate to $H_2O_2^+$ in strongly acid solutions,[40] but since the solutions we deal with have pH > 6, we do not consider this protonation. We must, however, include the ionization and ion-recombination reactions for the perhydroxyl radical HO_2

$$HO_2 \rightleftharpoons H^+ + O_2^- \tag{15}$$

and the corresponding reactions for HCO_3 and H_2CO_3. Rate constants are required for these ionization and ion-recombination reactions. A formula for estimating the rate constant for a diffusion-controlled reaction between charged particles in solution was given by Debye.[41,42] It predicts a value of about 10^{10} M^{-1} sec^{-1} for the reaction between H^+ and the anion of a weak acid. Measured protonation rate constants for a variety of bases are in fact several times 10^{10} M^{-1} sec^{-1}, except for OH^- and F^-, the rate constants for which are close to 10^{11} M^{-1} sec^{-1} .[36] Much lower values for the protonation rate constant are found for some organic bases, in which protonation involves a reorganization of the charge on the ion. For $\cdot O_2^-$, $\cdot CO_3^-$, and HCO_3^-, we estimate the rate constant for recombination with H^+ as 5×10^{10} M^{-1} sec^{-1}. Then the rate constant for ionization is calculated as 5×10^{10} multiplied by the acid ionization equilibrium constant. The rate constants used for the ionization and recombination reactions are shown in Table 3.

TABLE 3: Rate Constants Used for Ionization and Recombination Reactions

number	reaction	rate constant
20	$H^+ + OH^- \rightarrow H_2O$	$k_{20} = 1.3 \times 10^{11}$ M^{-1} s^{-1}
21	$H_2O \rightarrow H^+ + OH^-$	$k_{21} = 2.36 \times 10^{-5}$ s^{-1}
51	O_2- $+H^+ \rightarrow HO_2$	$k_{51} = 5 \times 10^{10}$ M^{-1} s^{-1}
52	$HO_2 \rightarrow O_2$- $+H^+$	$k_{52} = 9.98 \times 10^5$ s^{-1}
53	$\cdot CO_3^- + H^+ \rightarrow HCO_3$	$k_{53} = 5 \times 10^{10}$ M^{-1} s^{-1}
54	$HCO_3 \rightarrow CO_3^- + H^+$	$k_{54} = 1.26 \times 10^2$ s^{-1}
55	$HCO_3^- + H^+ \rightarrow H_2CO_3$	$k_{55} = 5 \times 10^{10}$ M^{-1} s^{-1}
56	$H_2CO_3 \rightarrow HCO_3^- + H^+$	$k_{56} = 2.20 \times 10^4$ s^{-1}

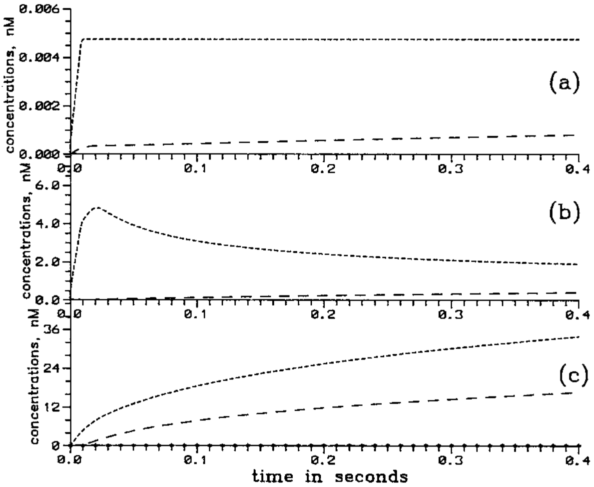

Figure 6. Results of simulation calculation, corresponding to $k_0 = 10^{-8}$ sec^{-1}, original $[HCO_3^-] = 5 \times 10^{-8}$ M, original $[O_2] = 5.55 \times 10^{-6}$ M (100 ppb). Calculated concentrations are in nM. (a) Upper curve is $[\cdot H]$, lower curve is $[\cdot CO_3^-]$. (b) Upper curve is $[\cdot OH]$, lower curve is $[H\cdot CO_3]$. (c) Top curve is $[\cdot O_2^-]$, dashed curve is $[H_2O_2]$, dots show $[H\cdot O_2]$.

Figures 6 and 7 show the results of a typical calculation, corresponding to $k_0 = 10^{-8}$ sec^{-1}, original $[HCO_3^-] = 5 \times 10^{-8}$ M, original $[O_2] = 5.55 \times 10^{-6}$ M (100 ppb). Note that air-saturated solutions have $[O_2] = 2.5 \times 10^{-4}$ M.[28] The concentration of $H\cdot$ (Figure 6a) rises rapidly to about 4.8×10^{-12} M and remains at this value. That of $\cdot OH$ (Figure 6b) rises rapidly to about 4.8×10^{-9} M, but then decreases almost as rapidly because of reactions with other constituents of the solution. The concentrations of $\cdot O_2^-$, H_2O_2, and $\cdot HO_2$ increase

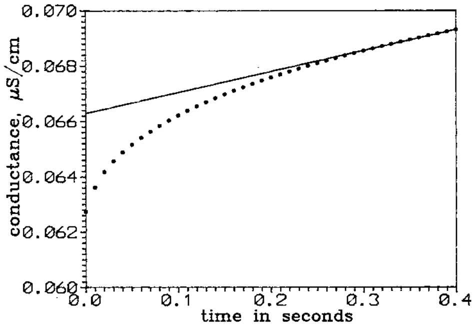

Figure 7. Conductance as a function of time, calculated from the concentrations shown in Figure 6. Solid line is linear fit to the results for t ≥ 0.3 s. The value of this line at $t = 0$, minus the conductance before irradiation, gives the conductance step.

monotonically (Figure 6c), but [$\cdot HO_2$] remains very small because $\cdot HO_2$ dissociates rapidly to H^+ and $\cdot O_2^-$. The hydrogen ion concentration increases constantly from its original value of 1.284×10^{-7} M, in concert with the increase in [$\cdot O_2^-$], and, because of the water autoioionization equilibrium, [OH^-] decreases constantly. The concentrations of bicarbonate and carbonic acid hardly change, but the concentrations of $\cdot CO_3^-$ and $H\cdot CO_3$ increase monotonically (Figures 6a and 6b). The rate constants are large enough so that equilibrium is essentially established in 0.1 s for all of the acid ionization reactions except $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$. In this case, the equilibrium product $[H^+][HCO_3^-]/[H_2CO_3]$ is equal to 2.86×10^{-10} after 0.4 s, as compared to the equilibrium constant, 2.51×10^{-10}.

The conductivity (Figure 7) increases rapidly at first, and then less rapidly. The increase in conductivity is due mainly to the increases in [H^+] and [$\cdot O_2^-$], since $\cdot CO_3^-$ makes a negligible contribution to the conductivity. The conductivity does not level off to a steady state, but approaches a line of positive slope. This constant increase in conductivity after several tenths of a second reflects the constant rate of production of HO_2, which dissociates to H^+ and O_2^-. The increase in [H^+] is accompanied by a decrease in [OH^-] because of the water autoionization equilibrium, but the conductivity increases because the specific conductivity of H^+ is higher than that of OH^-. Presumably, the rate of increase of conductivity with time would decrease when [O_2] decreased substantially; this would occur earlier for smaller $[O_2]_0$, larger k_0, and larger $[HCO_3^-]_0$. To calculate a step in conductivity for comparison with experiment, we have fitted the conductivity between 0.3 and 0.4 s to a line, as shown in Figure 7. The intercept of this line with the conductivity axis (equal to 0.0663 μS/cm in Figure 7), minus the conductivity before irradiation, is identified with the lamp step in conductivity measured in our experiments.

A large number of calculations were performed, for various concentrations of O_2 H_2 and HCO_3^-, and for various values of k_0. For each, the conductance from 0.3 to 0.4 s was fitted to a line, and the value at time 0 was subtracted from the *y*-intercept to give the conductance step. The original conductances (before irradiation) were 0.0627322 μS/cm for $[HCO_3^-]_0 = 5.0 \times 10^{-8}$ M and 0.117892 μS/cm for $[HCO_3^-]_0 = 2.5 \times 10^{-7}$ M. With $[O_2]_0 = 5.55 \times 10^{-8}$ and $[H_2]_0 = 0$, the steps in conductance due to irradiation were 0.00357 μS/cm for $[HCO_3^-]_0 = 5.0 \times 10^{-8}$ M and 0.00495 μS/cm for $[HCO_3^-]_0$ five times higher. The step is thus only weakly dependent on $[HCO_3^-]_0$.

TABLE 4: Intercepts and Slopes of Calculated Conductivity Plots

k_0 s^{-1}	$[O_2]_0$ M	$[HCO_3^-]_0$ M	intercept μS cm^{-1}	slope μS cm^{-1} sec^{-1}
$1.0\%10^{-8}$	$1.665\%10^{-8}$	$5.0\%10^{-8}$	0.06303	0.01070
$1.0\%10^{-8}$	$5.55\%10^{-8}$	$5.0\%10^{-8}$	0.06404	−0.00014
$1.0\%10^{-8}$	$1.11\%10^{-7}$	$5.0\%10^{-8}$	0.06487	−0.00012
$1.0\%10^{-8}$	$2.775\%10^{-7}$	$5.0\%10^{-8}$	0.06659	0.01236
$1.0\%10^{-8}$	$1.11\%10^{-6}$	$5.0\%10^{-8}$	0.06632	0.05480
$1.0\%10^{-8}$	$1.665\%10^{-6}$	$5.0\%10^{-8}$	0.06632	0.06295
$1.0\%10^{-8}$	$2.775\%10^{-6}$	$5.0\%10^{-8}$	0.06630	0.06985
$1.0\%10^{-8}$	$3.885\%10^{-6}$	$5.0\%10^{-8}$	0.06630	0.07322
$1.0\%10^{-8}$	$5.55\%10^{-6}$	$5.0\%10^{-8}$	0.06629	0.07577
$1.0\%10^{-8}$	$7.77\%10^{-6}$	$5.0\%10^{-8}$	0.06628	0.07723
$1.0\%10^{-8}$	$1.11\%10^{-5}$	$5.0\%10^{-8}$	0.06628	0.07880
$1.0\%10^{-8}$	$5.55\%10^{-6}$	$2.5\%10^{-7}$	0.12284	0.09380
$1.0\%10^{-8}$	$1.11\%10^{-5}$	$2.5\%10^{-7}$	0.12284	0.08978

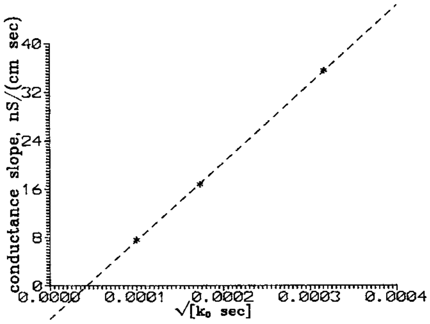

Figure 8. Calculated conductivity slopes plotted against square root of k_0. A best-fit line is shown.

The values of the slope and intercept of the conductivity plots, for a number of different inital conditions, are given in Table 4. It is seen that the conductivity step is essentially independent of [O_2] when [O_2] is significantly larger than $[HCO_3^-]_0$. This is in agreement with the experimental results. The reason is that the amount of $H\cdot O_2$ generated depends on the rate constant k_0, and only a small fraction of the O_2 present is converted to $H\cdot O_2$ in any case (the concentration of O_2 does not change noticeably in 0.4 s). For values of $[O_2]_0$ comparable to $[HCO_3^-]_0$, the step increases rapidly with $[O_2]_0$. (For very low values of $[O_2]_0$, a steady state is actually attained, since the oxygen is mostly depleted.) The step is negative for $[HCO_3^-]_0 \gg [O_2]_0$, so that it must cross the axis for some small value of $[O_2]_0$. The experimental data (Figure 5) seem to show a crossing at 0.0001 μM, but it must be remembered that the crossing point depends on the bicarbonate concentration.

The step increases as a function of irradiation intensity (k_0), but not at all proportionally. For $[O_2]_0 = 5.55 \times 10^{-6}$ M, $[HCO_3^-]_0 = 5.0 \times 10^{-8}$ M, and $k_0 = 1.0 \times 10^{-8}$, 3.0×10^{-8}, and 1.0×10^{-7} sec^{-1}, the intercepts are 0.066285, 0.071297, and 0.086755 μS/cm, respectively. The corresponding slopes are 0.0075766, 0.0167325, and 0.0355077 μS cm^{-1} sec^{-1}, so that the slopes increase much more rapidly with k_0 than do the intercepts. As shown in Figure 8, the conductivity slope is closely proportional to the square root of k_0 for the range of k_0 considered. The best-fit line

$$\text{conductivity } (\text{nS}^{-1}\ \text{sec}^{-1}\ \text{cm}^{-1}) = 129463\ \sqrt{(k_0\ \text{sec})} - 5.49772$$

fits the data with $r^2 = 0.99986$. Of course, the slope must become zero for $k_0 = 0$; the points in the figure already show some concavity upward. Proportionality to the square root of a rate constant is characteristic of dissociation reactions.

The effect of molecular hydrogen has also been investigated. Spinks and Woods[27] note that, although H_2 is a product of radiolysis, it usually plays a minor role because it escapes from solution and because its reaction rate constants are low, e.g., $H_2 + \cdot OH \rightarrow H\cdot + H_2O$ has $k = 4.9 \times 10^7$ M^{-1} sec^{-1}, whereas a saturated solution has $[H_2] = 7.8 \times 10^{-4}$ M. However, they

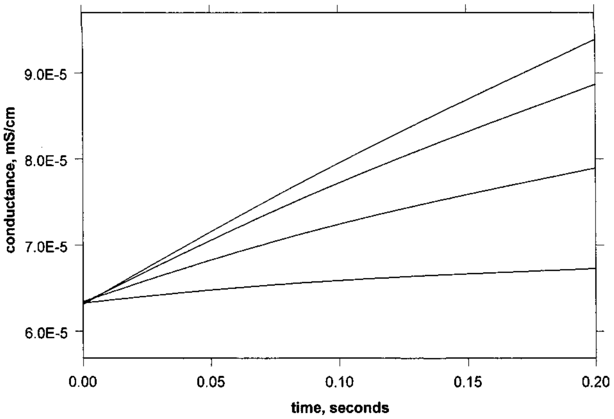

Figure 9. Calculated conductance as a function of time for solutions having $[O_2]_0 = 5.55 \times 10^{-6}$ M, $[\text{bicarbonate}]_0 = 5 \times 10^{-8}$ M, and different $[H_2]_0$. From bottom to top, curves correspond to $[H_2]_0 = 0$, 5.55×10^{-7} M, 1.665×10^{-7} M, and 2.775×10^{-7} M.

also state that "this reaction is significant if pure water is irradiated in a closed system, since it contributes to the back reactions keeping the net decomposition low." We studied the effect of dissolved hydrogen, by integrating the equations with and without H_2 present, giving the results in Figures 9 and 10. In all cases, $k_0 = 10^{-8}$, $[O_2]_0 = 5.55 \times 10^{-6}$ M, and $[HCO_3^-]_0 = 5 \times 10^{-8}$ M, so that the conductance before irradiation was 0.0627322 μS/cm.

In Figure 9, conductances are plotted as a function of time for $[O_2]_0 = 1.11 \times 10^{-7}$ and the four values of $[H_2]_0$: 0, $[O_2]_0/10$, $3[O_2]_0/10$, and $[O_2]_0/2$. Apparently, dissolved hydrogen increases the conductivity markedly. To understand the reason for this, species concentrations as a function of time were examined. Figure 10 shows the concentrations of O_2^-, H_2O_2, and OH for two runs in which the initial hydrogen concentration was 0 (dashed curves) and 2.775×10^{-6} M (solid curves). The increase in conductance on irradiation (top plots) is more than twice as great when hydrogen is present as when it is absent. The conductance plots (Figure 9) are paralleled by the plots of O_2^- concentration. However, the plots of $[H_2O_2]$ show the reverse behavior: $[H_2O_2]$ rapidly becomes much greater in the absence of hydrogen than in its presence. The hydroxyl concentration is also greatly decreased by the presence of hydrogen. The concentration of $\cdot$H is not shown; it is in the picomolar range because it is so reactive, but is much higher in the presence of H_2 (although it quickly drops off from its value just after irradiation begins).

Thus, in the presence of hydrogen, oxygen is converted more efficiently to superoxide anion, and the increase in $[O_2^-]$ is responsible for the increase in the conductivity. The explanation for the enhanced production of O_2^- is found in the plots of $[H\cdot]$ and $[\cdot OH]$ as a function of time. Superoxide comes from perhydroxyl radical $H{\cdot}O_2$, which is produced by the addition of $\cdot$H to O_2. The concentration of hydroxyl, which is 3 orders of magnitude larger than that of H$\cdot$, is much higher in the absence of H_2 than in its presence, and $\cdot$OH lowers superoxide concentration because it can react with $H{\cdot}O_2$ to re-form O_2. Thus the H_2 enhances $[O_2^-]$ by converting $\cdot$OH to H$\cdot$ according to: $\cdot OH + H_2 \rightarrow H\cdot + H_2O$. Spinks and Woods[28] suggest that the reaction of $\cdot$OH with H_2 will not compete with other reactions of $\cdot$OH at smaller H_2 concentrations than the saturation value, $[H_2] = 7.8 \times 10^{-4}$ M, but our results show that this reaction is of primary importance in the situation being considered.

VII. Calculated Effect of Stopping Irradiation

Experiments (Figures 2−4) show that, when irradiation is cut off, the conductivity drops off but never returns to its value before the irradiation was turned on. In experiments such as that of Figures 2 and 4, the lamp steps are superimposed on a constantly increasing conductivity baseline, mainly due to the increase in cell temperature, and possibly also because electrolysis continues, oxidizing carbon to bicarbonate. This, however, does not explain the large difference between the conductivity after the first on−off sequence (before the lamp is turned on again) and the conductivity before irradiation is begun.

To understand the reason for this difference, we performed simulations in which the lamp was turned on at time 0, left on for 0.4 s, and then turned off and left off for 0.2 s. This was accomplished by integrating the differential equations with a nonzero value of k_0 for 0.4 s and then, starting from the concentrations obtained at 0.4 s, integrating the same differential equations with $k_0 = 0$. As observed experimentally, the conductivity drops off rapidly when the irradiation is cut off, but to a value significantly above the value it had before irradiation was begun. Results from such a calculation are shown in Figures 11 and 12. At time 0, the concentration of bicarbonate was 5×10^{-8} M, the concentration of oxygen was 1.11×10^{-7} M, and no hydrogen was present.

Figure 11a shows the calculated conductance as a function of time. It rises rapidly from 62.7 nS/cm to 64.9 nS/cm in response to turning the lamp on. As found experimentally, it drops off rapidly when the lamp is turned off, but only to 64.2 nS/cm. As shown in Figure 11b, the primary species produced by the irradiation, $\cdot$H and $\cdot$OH, disappear rapidly when

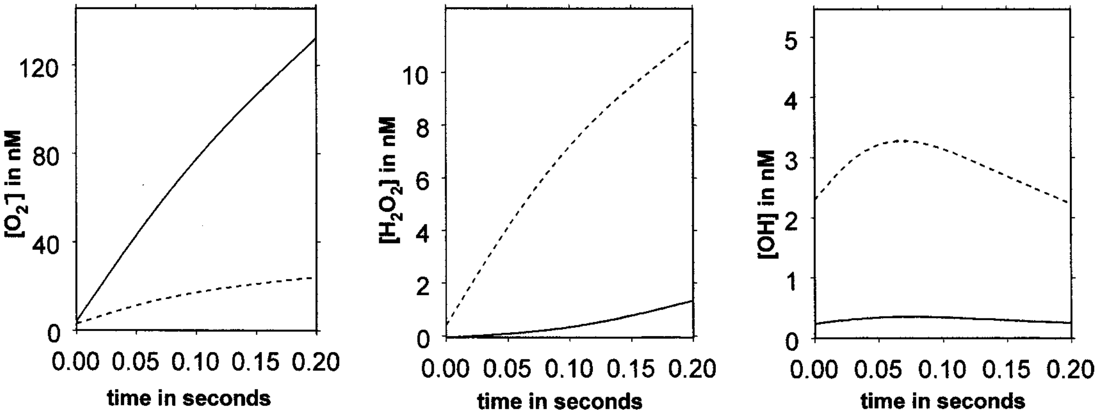

Figure 10. Species concentrations as a function of time from simulations with $[O_2]_0 = 5.55 \times 10^{-6}$ M and $[\text{bicarbonate}]_0 = 5 \times 10^{-8}$ M, with and without hydrogen. Dashed curves are for no hydrogen originally present, solid curves for $[H_2]_0 = 2.775 \times 10^{-7}$ M.

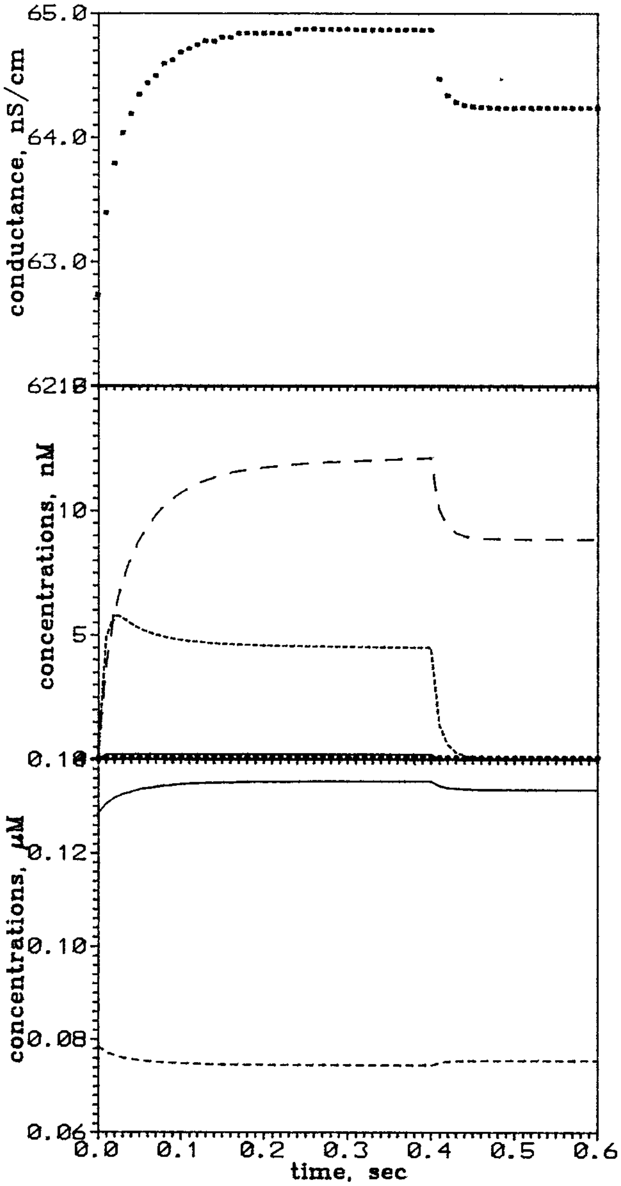

Figure 11. Results of simulation with $[HCO_3^-] = 5 \times 10^{-8}$ M, $[O_2]_0 = 1.11 \times 10^{-7}$M, and $[H_2]_0 = 0$. (a) Calculated conductance as a function of time. (b) Concentrations of $\cdot O_2^-$ (long-dashed curve), $\cdot OH$ (short-dashed curve), $\cdot H$ (solid curve), and $H\cdot O_2$ (dots) as functions of time. (c) Concentrations of H^+ (solid curve) and OH^- (dashed curve) as functions of time.

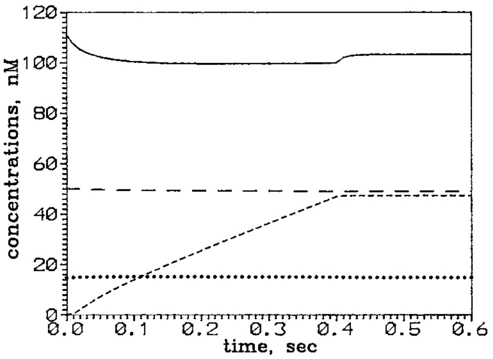

Figure 12. Concentrations of other species from the simulation of Figure 11. Solid curve is $[O_2]$, long-dashed curve is $[HCO_3^-]$, short-dashed curve is $[H_2O_2]$, dotted curve is $[H_2CO_3]$.

irradiation is interrupted (the concentration of H never exceeds 2.1×10^{-10} M during irradiation in any case), but O_2^- and HO_2, created during irradiation by the reaction of H with O_2, persist. Equilibrium with respect to the reaction $HO_2 \rightleftharpoons H^+ + O_2^-$ is maintained as $\cdot O_2^-$ disappears, but the disappearance is very slow because superoxide is destroyed by reaction with HO_2, whose concentration is very low. The superoxide ion and the hydrogen ion, whose concentration must increase to maintain electroneutrality, are responsible for the increased conductivity with the lamp off.

The decrease in hydrogen ion concentration when irradiation is stopped is accompanied by an increase in hydroxide ion concentration because of the water autoionization equilibrium (Figure 11c). Figure 12 shows concentrations of some other species. The concentration of O_2, which is converted into O_2^- by irradiation, decreases when irradiation starts and increases when it stops, but without returning to its value before irradiation. The concentrations of HCO_3^- and H_2CO_3 are largely unaffected by starting or stopping irradiation. Hydrogen peroxide is produced at an essentially constant rate while the radiation is on and at a negligible rate while the radiation is off.

In our final illustrations, we assume continuous generation of bicarbonate ion, which leads to a continuous increase in conductivity. This is to model the increase in background conductivity observed in our experiments; a typical value for d*c*/d*t* is 0.00125 μS cm^{-1} sec^{-1}. The increase is actually due mostly to the increase in cell temperature, but, if the solution being irradiated contains oxidizable carbon, there will in fact be continuous generation of bicarbonate from the oxidizable carbon.

If only H^+, OH^-, and HCO_3^- are taken into account, it is easy to show that

$$[H^+] = \frac{1}{2}\{[HCO_3^-] + \sqrt{[HCO_3^-]^2 + 4.028 \times 10^{-14}}\}$$

so that $[H^+] \cong [HCO_3^-]$ when $[HCO_3^-]$ exceeds a few times 10^{-7}. The conductance in S cm^{-1} is $0.0445[HCO_3^-] + 0.3496[H^+] + 0.1991[OH^-]$ so that we have for the rate of change of conductance c with time

$$\frac{dc}{dt} = \left(0.3941 - \frac{2.005\times10^{-15}}{[HCO_3^-]^2}\right)\frac{d[HCO_3^-]}{dt} \qquad (16)$$

To get $dc/dt = 0.00125$ μS cm^{-1} sec^{-1} at $[HCO_3^-] = 2 \times 10^{-7}$ M, $d[HCO_3^-]/dt$ must be 3.63×10^{-9} M/sec. We thus add oxidation of methanol to H_2CO_3 (which dissociates to $[HCO_3^-]$) at this rate into our differential equations. However, the oxidation must be accompanied by a reduction of some other substance. We assume reduction of water to hydrogen according to

$$H_2O + e^- \rightarrow OH^- + {}^1/_2\, H_2$$

Combining this with the oxidation reaction

$$CH_3OH + 2H_2O \rightarrow H_2CO_3 + 6e^- + 6H^+$$

we obtain the overall reaction

$$8H_2O + CH_3OH \rightarrow H_2CO_3 + 6H^+ + 6OH^- + 3H_2$$

This means that the rate of creation of H_2 should be three times the rate of creation of H_2CO_3, and the rate of creation of H^+ and OH^- should be twice the rate of creation of H_2. Most of the H^+ and OH^- will combine to H_2O in any case.

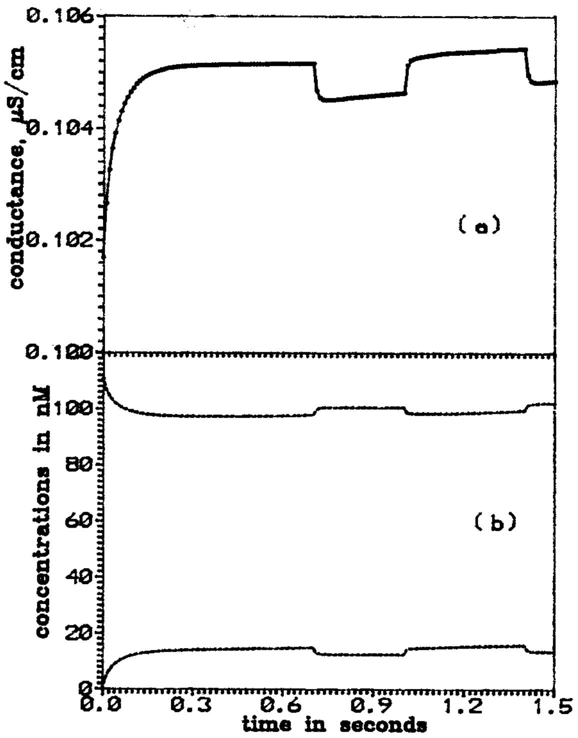

Figure 13. Results from a simulation involving two on−off lamp cycles, and including constant addition of H_2CO_3 at 3.63 × 10^{-9} M/sec, of H_2 at 1.089 × 10^{-8} M/sec, of H^+ at 2.178 × 10^{-8} M/sec, and of OH^- at 1.089 × 10^{-8} M/sec. The additions are to simulate the constant increase in background conductance, actually due to increase in cell temperature. (a) Conductivity as a function of time. (b) Concentrations of O_2 (upper curve) and $\cdot O_2^-$ (lower curve) as functions of time.

Figure 13 shows the results from a simulation in which $[H_2CO_3]$, $[H^+]$, and $[OH^-]$ were assumed to be generated constantly, with the lamp being turned on and off twice. The original concentrations of O_2, H_2, and HCO_3^- were 1.11 × 10^{-7} M, 1.665 × 10^{-7} M, and 2 × 10^{-7} M, respectively. The original conductance was 0.101684 μS/cm. A constant term of 3.63 × 10^{-9} M/sec was added into $d[H_2CO_3]/dt$, 1.089 × 10^{-8} M/sec was added to $d[H_2]/dt$, and 2.178 × 10^{-8} M/sec was added into $d[H^+]/dt$ and $d[OH^-]/dt$. The lamp was stepped on ($k_0 = 1 \times 10^{-8}$ sec^{-1}) at time 0, left on for 0.7 s, turned off and kept off ($k_0 = 0$) for 0.3 s, turned on again ($k_0 = 1 \times 10^{-8}$ sec^{-1}) for 0.4 s, and turned off for the remaining 0.1 s.

As seen in Figure 13a, the conductance rises to about 0.1051 μS/cm the first time the radiation is turned on, continues to rise slowly during irradiation, and drops quickly to 0.1045 μS/cm when the radiation is turned off. It rises slowly with the irradiation off, increases rapidly to 0.1053 μS/cm the second time the irradiation is turned on, continues to rise slowly durng irradiation, and drops to 0.1048 μS/cm the second time the irradiation is turned off. The slow increase during periods of constant irradiation or zero irradiation is due to the increase in $[HCO_3^-]$, arising from the H_2CO_3, which was explicitly put into these calculations. However, the major contributor to the increased conductivity after the first on−off step is due to the O_2^- generated by the reaction of O_2 with radiation-produced H. The plot of $[O_2^-]$ vs time (Figure 13b) in fact strongly resembles the conductance plot. The oxygen concentration plot is the mirror image of the $[O_2^-]$ plot, so that the sum, $[O_2] + [O_2^-]$, is essentially constant. The bicarbonate concentration is found to vary much less than the superoxide concentration, and the concentrations of H^+ and OH^- even less than $[HCO_3^-]$. Variations in $[H^+]$ and $[OH^-]$ are required to maintain electroneutrality and the value of the product $[H^+][OH^-]$.

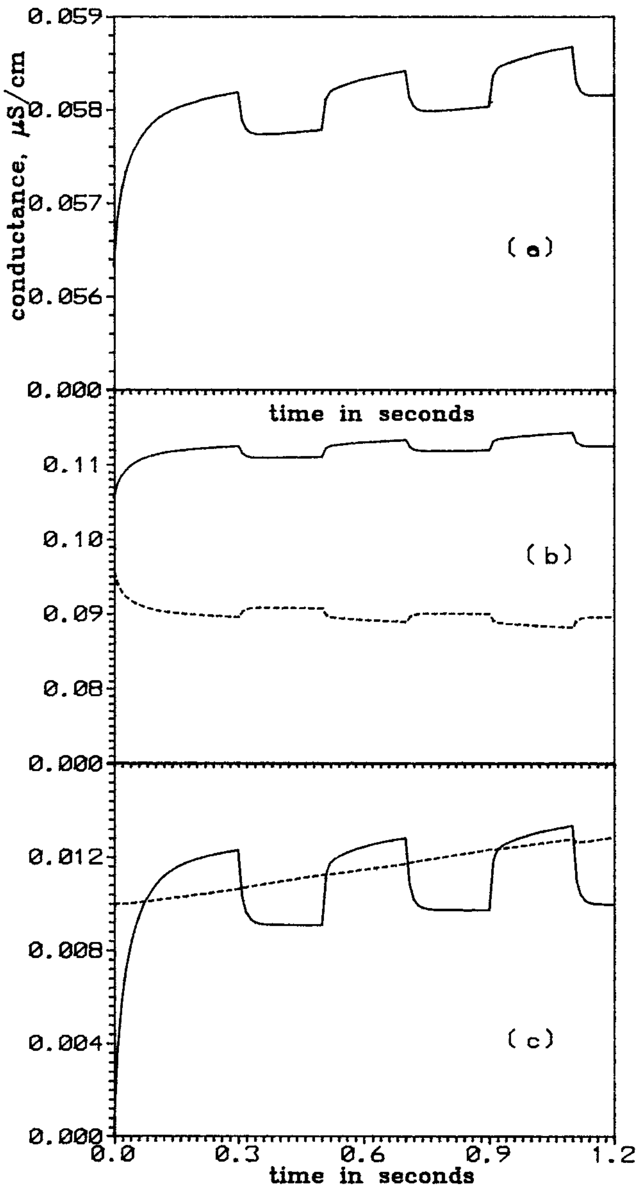

Figure 14. Results of simulation involving three on−off lamp cycles, and including constant addition of H_2CO_3 at 3.63 × 10^{-9} M/sec, of H_2 at 1.089 × 10^{-8} M/sec, of H^+ at 2.178 × 10^{-8} M/sec, and of OH^- at 1.089 × 10^{-8} M/sec. Original concentrations were $[O_2]_0 = 1.11 \times 10^{-7}$ M, $[H_2]_0 = 0$ M, and $[HCO_3^-]_0 = 1 \times 10^{-6}$ M. (a) Calculated conductance as a function of time. (b) Calculated concentrations of H^+ (solid curve) and OH^- (dashed curve) as functions of time. (c) Calculated concentrations of $\cdot O_2^-$ (solid curve) and HCO_3^- (dashed curve) as a function of time.

The next simulation began with concentrations of O_2, H_2, and HCO_3^- of 1.11 × 10^{-7} M, 0, and 1 × 10^{-8} M, respectively. The original conductivity was 0.056328 μS/cm. A constant term of 3.63 × 10^{-9} M/sec was added into $d[H_2CO_3]/dt$, 1.089 × 10^{-8} M/sec was added to $d[H_2]/dt$, and 2.178 × 10^{-8} M/sec was added into $d[H^+]/dt$ and $d[OH^-]/dt$. The lamp was stepped on ($k_0 = 1 \times 10^{-8}$ sec^{-1}) at time 0, left on for 0.3 s, turned off and kept off ($k_0 = 0$) for 0.2 s, turned on again ($k_0 = 1 \times 10^{-8}$ sec^{-1}) for 0.2 s, turned off for 0.2 s, turned on for 0.2 s, and turned off for the remaining 0.1 s. The calculated conductivity (Figure 14a) shows the expected sawtooth pattern as a function of time. There is a sharp rise each time the lamp is turned on and a rapid decrease each time the lamp is turned off. After each on or off step, the conductivity approaches a line of positive slope, due to the continued production of HCO_3^-, H^+, and OH^-. After the lamp is turned off at 0.3 s, the conductivity decreases to about 0.058 μS/cm, much higher than it was before irradiation. This must be due to the presence of long-lived species produced by the irradiation, which contribute significantly to the conductance. Since the concentration of $\cdot CO_3^-$ never exceeds several picomolar, one must look at the species H^+, OH^-, HCO_3^-, and $\cdot O_2^-$.

Figure 14b shows the concentrations of H^+ and OH^- as a function of time. They follow the conductivity steps closely, $[H^+]$ increasing and $[OH^-]$ decreasing when the lamp is turned on. The product of $[H^+]$ and $[OH^-]$ always remains close to 1.007×10^{-14}, the water ionization equilibrium constant. Figure 14c shows the concentrations of HCO_3^- and O_2^-. The former shows a continuous increase, due to the production of HCO_3^- assumed in the model. The pattern for $[O_2^-]$ closely resembles the pattern for the conductivity, except that the apparent baseline when the lamp is off is horizontal. The concentration of O_2^- increases rapidly during irradiation and decreases when the lamp is turned off off, but to a slightly higher level after each lamp on−off sequence. The concentration of the parent O_2 does the reverse of that of $\cdot O_2^-$, since $\cdot O_2^-$ is generated from O_2. Again we see that the long-lived species generated by the radiation, and responsible for the fact that the conductivity never falls back to its original value, is $\cdot O_2^-$.

The $\cdot O_2^-$ species is long lived because it disappears[38,39] by reaction with HO_2 ($\cdot O_2^-$ does not react with itself) and the concentration of HO_2 is always less than 0.013 times that of $\cdot O_2^-$. The pK of HO_2 is 4.7;[39] in fact, the calculated reaction quotient $[H^+][O_2^-]/[HO_2]$ is equal to 1.995×10^{-5} or $10^{-4.7}$ to a few parts in a thousand except during the first few hundredths of a second after a step. The concentration of H_2O_2 increases as a result of irradiation, reaching 0.2 μM at 1.2 s, but the rate constant for the reaction of $\cdot O_2^-$ with H_2O_2 is only 2.25[43] so we have not considered this reaction.

A final series of calculations for which we present results had original concentrations of O_2, H_2, and HCO_3^- of 1.11×10^{-7} M, 1.665×10^{-7} M, and 2×10^{-7} M, respectively. Again, a constant term of 3.63×10^{-9} M/sec was added into $d[HCO_3^-]/dt$, 1.089×10^{-8} M/sec was added to $d[H_2]/dt$, and 2.178×10^{-8} M/sec was added into $d[O_2]/dt$. The lamp was stepped on ($k_0 = 1 \times 10^{-8}$ sec^{-1}) at time 0, left on for 0.3 s, turned off and kept off ($k_0 = 0$) for 0.2 s, and then the cycle of 0.2 s on ($k_0 = 1 \times 10^{-8}$ sec^{-1}) and 0.2 s off was repeated two more times. The calculated conductance (Figure 15) does not change much because the concentrations of O_2, H_2, and HCO_3^- are small and almost the same, and their effects tend to cancel. Note, however, the atypical shape of the conductance curve from 0 to 0.3 s. Study of the curves of species concentrations vs time reveals that this is because of the continuous addition of bicarbonate.

Initially, $[O_2]$ exceeds $[HCO_3^-]$, so that superoxide forms before $H\cdot CO_3$ and $\cdot CO_3^-$ do, causing the initial conductance increase. (Indeed, oxygen prevents formation of $H\cdot CO_3$ because superoxide can reduce $H\cdot CO_3$ to HCO_3^-.) As $[HCO_3^-]$ increases, more is converted to $\cdot CO_3^-$, which decreases the conductance. As always, the main contributor to the conductance is H^+, and $[H^+]$ depends on the concentrations of HCO_3^- and $\cdot O_2^-$. The oxygen concentration shows a constant increase due to the explicit addition of O_2, on which are superimposed decreases when the lamp is turned on and increases when it is turned off. The decreases result from conversion of $[O_2]$ to $[\cdot O_2^-]$ and the increases from the reverse.

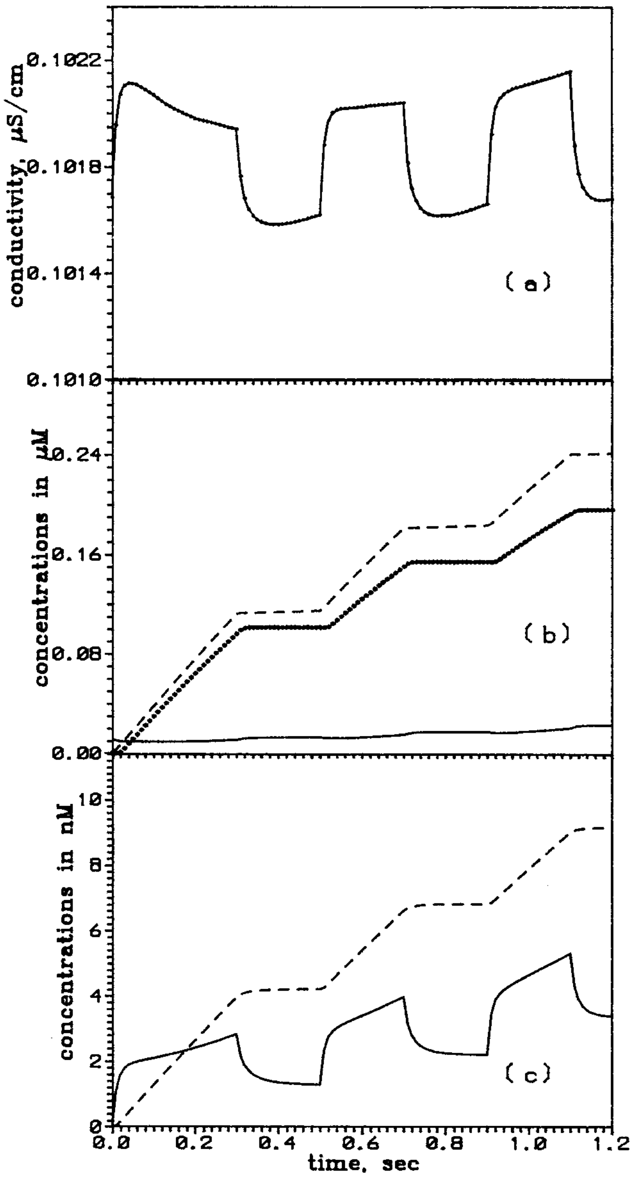

Figure 15. Results of simulation involving three on−off lamp cycles, and including constant addition of H_2CO_3 at 3.63×10^{-9} M/sec, of H_2 at 1.089×10^{-8} M/sec, of H^+ at 2.178×10^{-8} M/sec, and of OH^- at 1.089×10^{-8} M/sec. Original concentrations were $[O_2]_0 = 1.11 \times 10^{-7}$ M, $[H_2]_0 = 1.665 \times 10^{-7}$ M, and $[HCO_3^-]_0 = 2 \times 10^{-7}$ M. (a) Conductivity as a function of time. (b) Concentrations of various species. From top to bottom, the curves represent $[H_2]$, $[H_2O_2]$, and $[O_2]$. (c) Concentrations of $\cdot O_2^-$ (solid curve) and $H\cdot CO_3$ (dashed curve).

VIII. Discussion and Conclusions

In this article, we have presented experimental results for conductivities of irradiated ultrapure water containing known small concentrations of dissolved oxygen, hydrogen, and bicarbonate. The conductivities were measured in a cell designed and used for measurement of total oxidizable carbon. In that application, water flows continuously through the cell, and dissolved carbon (assumed to be in the form of methanol) is oxidized to bicarbonate by ultraviolet radiation (wavelength 185 nm). The resultant increase in conductivity is interpreted to give the total oxidizable carbon concentration. For conductivity measurements, the water was trapped in the cell, and the ultraviolet lamp was turned on and off several times. The rapid increase (sometimes decrease) in conductivity which followed turning on the lamp was studied, as well as the change in the opposite direction which followed turning it off. The dependence of these "lamp steps" on the concentrations of dissolved oxygen, hydrogen, and bicarbonate was measured.

A model was proposed to explain these results in terms of the reactions occurring in very pure water, starting from the radiation-induced dissociation of water into hydrogen and hydroxyl radicals. The model included a number of known reactions between these radicals, bicarbonate ion, hydrogen, oxygen, and reaction products. Rate constants for almost all these were available in the literature, but for a few of them rate constants were estimated. Rate constants in the literature were also used to limit the number of reactions considered. The differential equations for the rate of change of concentrations of various species were generated and integrated. From the concentrations we calculated conductivity as a function of time and initial concentrations. The calculated changes in conductivity agreed semiquantitatively with the changes measured experimentally.

The agreement with experiment so far obtained gives us confidence in our model. We are able to decide which reactions, and which short-lived species, are important and which can be neglected. This will be important in future work, in which we will extend the model to consider additional carbon-containing species. Of course, one could include additional reactions, or substitute other reactions for some of the ones we have included in our model, without hurting the agreement between theory and experiment. This simply means that a model or theory cannot be proved, only disproved when it fails to explain experimental results. The model presented here is consistent with our experimental results and with what is already known about the results of irradiating water, as found in the literature.

It is assumed that the primary event caused by irradiation is the formation of hydrogen and hydroxyl radicals from water. Although solvated electrons can be produced in water by X-ray and higher-energy radiation, they cannot be produced in substantial amounts by ultraviolet radiation. We do not find it necessary to include any reactions that produce solvated electrons from other radical species, so solvated electrons are not considered at all in our model. We in fact carried out calculations with a much more complicated model, which included formation and destruction of solvated electrons. The results (not shown here) show that concentrations of the important species were hardly changed, justifying our neglect of solvated electrons.

The hydrogen radical is a reducing agent and the hydroxyl radical is an oxidizing agent. If oxygen is present, $\cdot H$ can reduce it to $H\cdot O_2$, (rate constant 2.1×10^{10} M^{-1} sec^{-1}); $H\cdot O_2$ dissociates to H^+ and superoxide radical, $\cdot O_2{}^-$, because the p*K* of perhydroxyl is only 4.7. The formation of ions leads to an increase in conductivity (positive lamp step). Since the main mechanism for destruction of superoxide is its reaction with $H\cdot O_2$, and the concentration of $H\cdot O_2$ is very small, the increase in conductivity persists for a long time after the radiation is turned off. The lamp step is no more than 10 nS/cm when $[O_2]$ increases by 3 orders of magnitude. This is because, when the concentration of $H\cdot O_2$ becomes large, reaction with hydroxyl radical to form O_2 (rate constant 6×10^9 M^{-1} sec^{-1}) or reaction with $\cdot H$ to form hydrogen peroxide (rate constant 10^{10} M^{-1} sec^{-1}) becomes important. Thus the superoxide concentration cannot increase too much.

If diatomic hydrogen is present, it can react with $\cdot OH$ to generate $\cdot H$ radicals. In the presence of O_2, this leads to enhanced formation of $H\cdot O_2$ and a higher conductivity step. More $H\cdot O_2$ is formed because the additional $\cdot H$ reacts with O_2, but also because $\cdot H$ removes $\cdot OH$, which could oxidize $H\cdot O_2$ back to O_2. Of course, $\cdot H$ can also destroy superoxide, reacting with $H\cdot O_2$ to form H_2O_2, hydrogen peroxide, or reacting with $O_2{}^-$ to form $H\cdot O_2{}^-$, the anion of hydrogen peroxide, but Figure 10 shows that this is not important: production of H_2O_2 is decreased when H_2 is present. Most of the H_2O_2 is produced by combination of hydroxyl radicals, which hydrogen radicals remove. The p*K* of H_2O_2 is too large for its ionization to contribute significantly to the conductivity. It may be noted that our reaction scheme does not include all of the reactions of H_2O_2, such as its decomposition on absorption of ultraviolet radiation. Its concentration never gets very high in the situations discussed so far.

If carbonic acid or bicarbonate is present in the irradiated solution, the hydroxyl radicals generated can oxidize it to $\cdot HCO_3$ or $\cdot CO_3{}^-$ respectively. The p*K* of $\cdot HCO_3$ (9.6) being significantly higher than that of H_2CO_3 (6.4), the effect is to reduce ionization and hence conductivity. This is what gives rise to a negative lamp step. The situation is changed when oxygen is present as well as bicarbonate, since the lamp step is in the opposite direction for oxygen. The relative amounts of bicarbonate and oxygen determine whether the lamp step is positive or negative.

Our model was developed to explain the following experimental results: (1) the conductivity *decreases* with ultraviolet irradiation if the concentration of dissolved oxygen is very low; (2) for positive conductivity steps, the size of the step increases with $[O_2]$, but not linearly—it apparently goes through a maximum; (3) dissolved hydrogen increases the conductivity step on irradiation; (4) the conductivity step increases with increased rate of irradiation (rate constant k_0), but not linearly. Of course H^+ or H_3O^+ is almost always the major contributor to conductivity because of its high specific conductivity, but the concentration of H^+ is determined by electroneutrality and by the concentrations of other species that react with H^+. Thus our explanations involve the species created by irradiation, starting with $H\cdot$ and $\cdot OH$.

With respect to (1), it seems to us impossible to get a radiation-induced decrease in conductivity for completely pure water. However, there is almost certainly a nonzero bicarbonate concentration in our samples, since their conductivity before irradiation is significantly higher than that calculated for completely pure water. Bicarbonate can be oxidized to $H\cdot CO_3$ by $\cdot OH$, and $H\cdot CO_3$ can release a proton to form the carbonate radical anion $\cdot CO_3{}^-$. Since the p*K* of $H\cdot CO_3$ (9.6) is much larger than that of H_2CO_3, the parent acid of bicarbonate, the effect of the formation of $H\cdot CO_3$ is to increase the pH and decrease the conductivity.

Reactions of the carbonate radical ion with enzymes are important;[44] in particular, it can rapidly inactivate the superoxide dismutases. It is produced from carbon dioxide by peroxynitrite, which itself is formed rapidly from nitric oxide and superoxide anion. Therefore, $\cdot CO_3{}^-$ must be considered in studies involving oxygen-containing free radicals generated by irradiation or chemical reaction.[45] Bisby et al.[46]give some of its electronic properties. They have recently suggested that the value of 9.6 for the p*K* of $\cdot CO_3{}^-$ is incorrect, and that $\cdot CO_3{}^-$ formed by oxidation of $HCO_3{}^-$ does not undergo protonation to $H\cdot CO_3$. If these suggestions were correct, the oxidation of $HCO_3{}^-$ to $\cdot CO_3{}^-$ would have little effect on the conductivity, since it would not lower the concentration of H^+, and our model would not explain the conductivity decrease of oxygen-free solutions with irradiation. On the other hand, there would be little consequence for solutions containing oxygen, since $[\cdot CO_3{}^-]$ is always many times greater than [$\cdot HCO_3$], the lack of protonation of $\cdot CO_3^-$ to $\cdot HCO_3$ would change the concentration of $\cdot CO_3^-$ only slightly. Recently, Bonini et al.[44] have directly detected $\cdot CO_3^-$ in aqueous solutions at physiological pH for the first time, using electron spin resonance.

(2) If oxygen is present, it can react with radiation-produced $\cdot H$ to form the perhydroxyl radical $H\cdot O_2$, which, as discussed above, ionizes readily to form H^+ and O_2^-, leading to a substantial increase in conductivity. Since superoxide is long-lived, the increase in conductivity persists for a long time after the radiation is turned off. In addition, the O_2^- formed counters the conductivity decrease caused by the oxidation of bicarbonate to $H\cdot CO_3$, since O_2^- can reduce the carbonate radical ion to bicarbonate, which increases the conductivity.

The superoxide radical ion is a subject of great current interest, particularly in biochemistry (for instance, ref 47). The structure of its hydration shell has recently been determined.[48] It can be a mild oxidant or reductant, as can HO_2, but does not react with most organic compounds.[2] It has recently been shown[49] that irradiation of titanium dioxide generates both singlet oxygen and superoxide anion, so that superoxide can be generated directly on the surface of titania, with which our electrodes are coated. However, the superoxide generated on electrode surfaces is expected to be less important in our experiments than that generated in solution.

Our calculations show that the positive step in conductivity on irradiation increases with oxygen concentration, but the slope of a graph of step size vs [O_2] decreases with oxygen concentration, in accord with the experimental results. The reason is that, as discussed above, the concentration of O_2^- is determined by competition between a number of reactions which create it or destroy it, and not by a simple equilibrium with O_2. Our model does not explain the decrease in the lamp step size with [O_2] at high concentrations, shown in Figure 5. We believe that it is due to the absorption of ultraviolet light by species other than water. The absorption effectively reduces k_0, since absorbed radiation does not produce the primary species $H\cdot$ and $\cdot OH$.

At $\lambda = 185$ nm, the absorption coefficient of oxygen gas ($P = 1$ atm, $T = 298$ K) is about[50] 1.1 cm^{-1}, so that the molar absorptivity is only about 25 M^{-1} cm^{-1}. The absorption coefficient of ozone is about 12.5, an order of magnitude higher than that of oxygen. In addition, both O_2^- and HO_2 absorb strongly in this region of the ultraviolet, the former having an absorption maximum at 245 nm ($\epsilon = 2000$ M^{-1} cm^{-1}) and the latter a maximum at 230 nm ($\epsilon = 1250$ M^{-1} cm^{-1}).[22] We estimate that, at 185 nm, the extinction coefficient for both species is about 800 M^{-1} cm^{-1}. Experimentally, the maximum in conductivity occurs for [O_2] near 10^{-6} M. If all the oxygen is transformed into superoxide, so that [O_2^-] $\approx 10^{-6}$ M, its contribution to the absorption coefficient would be 8×10^{-4} cm^{-1}.which is 0.0004 times the absorption coefficient of water (1.8 cm^{-1}). At higher concentrations, O_2^- might absorb enough to have a significant effect on k_0. Another species which could absorb ultraviolet radiation is hydrogen peroxide, formed by some of the reactions we have discussed.

(3) Experimentally, it is found that dissolved hydrogen increases the conductivity step when dissolved oxygen is present. Hydrogen can react with the $\cdot OH$ radicals produced from H_2O by irradiation ($H_2O \rightarrow H\cdot + \cdot OH$) acording to: $H_2 + \cdot OH \rightarrow H_2O + H\cdot$. As we have noted, it is the reaction of $H\cdot$ with O_2 to form $HO_2\cdot$ that is responsible for the conductivity step in the first place. Adding the three reactions just mentioned yields

$$H_2 + O_2 \rightarrow H\cdot + H\cdot O_2$$

and adding the reaction of $H\cdot$ with O_2 once more yields

$$H_2 + 2O_2 \rightarrow 2H\cdot O_2$$

Thus the presence of hydrogen augments, the production of hydroperoxyl radical, and hence, by producing more superoxide radical, increases the conductivity.

(4) Our model correctly predicts that the conductivity step increases with the intensity of radiation, but much less than proportionally. Since the initial radiation-induced reaction dissociates water to two species, one might expect proportionality to the square root of the intensity. This occurs in certain regimes, but the situation is complicated because of all the reactions undergone by the species produced directly from water, $H\cdot$ and $\cdot OH$. It may also be necessary to consider the effects of 185 nm radiation on species other than water, which we have not done.

The reaction system has been assumed to be homogeneous, but it is not. Conductivity measurements are performed in a cell in which oxidation and reduction occur on the electrodes. The electrode reactions contribute to the faradaic current. The diffusion of the products of these reactions from the electrodes into bulk solution, and of the reactants toward the electrodes, requires several seconds. However, judging from the size of the faradaic current, the effect is believed to be small. A more important reason for considering an inhomogeneous solution is to take into account the absorption of radiation by water. One should consider slabs of liquid at different depths z, with the value of k_0 (rate constant for production of $H\cdot$ and $\cdot OH$ from H_2O) decreasing exponentially with depth.

The cell used for the conductivity measurements is thought of as a box of dimensions a, b, and c in the x- y- and z-directions. The two electrodes are parallel to the $x-z$ plane and located at opposite faces of the box, i.e., at $y = 0$ and $y = b$. Illumination is from the top, in the z−direction, with the intensity of radiation being

$$I = I_o \exp[-\epsilon_w(c-z)]$$

where I_o is the intensity at $z = 0$ and the absorption coefficient of water, ϵ_w, is about 1.8 cm^{-1}. Since the conductivity will vary with z, and the voltage across the electrodes ΔV is fixed, the current density will depend on z:

$$j(z) = \kappa(z)\Delta V$$

The average current density is $(1/c)\int_0^c j(z)\,dz$, so that the apparent conductivity is the average, $(1/c)\int_0^c \kappa(z)\,dz$ (one here has conductors in parallel). In the present article, we calculate the average conductivity only; in a more accurate calculation, one would calculate conductivity κ as a function of I, convert to $\kappa(z)$, and integrate over z to get the average conductivity.

Before trying to get precise quantitative agreement between our calculations and results such as shown in Figure 2, we expect to study radiation-induced reactions involving carbon species. As noted at the beginning of the article, these are the species whose concentrations are measured by cells such as shown in Figure 1. Since electron transfer occurs one electron at a time, this requires adding to our model the reactions of at least seven carbon species, from CH_3OH (oxidation number of C = −2) to HCO_3^- (oxidation number +4). The additional number of reactions will make integrating the differential equations more difficult and time-consuming, presenting a significant challenge.

The results of the calculations presented here will be useful in deciding which reactions are important, and which may be safely neglected.

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