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Temperature Dependence of the Hydrogen Peroxide Production in the γ-Radiolysis of Water

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The radiation chemical yield of hydrogen peroxide has been determined in the γ-radiolysis of water at neutral pH. Methanol, ethanol, and bromide have been used as OH radical scavengers in order to explore the temporal dependence of hydrogen peroxide formation at elevated temperatures. The scavenger results at all temperatures confirm that OH radicals are the sole source of hydrogen peroxide at short times in the γ-radiolysis of water. Variation in dose rate by a factor of 20 shows no influence on the yield. With increasing temperature the yield of hydrogen peroxide is found to decrease, and the microsecond radiation chemical yields at low scavenger concentrations are found to be $G\ (H_2O_2) = 0.78-2.43 \times 10^{-3}$ T (°C) molecules/100 eV for methanol as a scavenger, and $G\ (H_2O_2) = 0.74-2.40 \times 10^{-3}$ T (°C) molecules/100 eV for bromide. The scavenger concentration dependence of the yields at elevated temperatures is discussed. Assuming an activation energy of 71 kJ mol^{-1} the thermal decomposition reaction rate constant for hydrogen peroxide in aqueous solution is estimated to be $6.5\ (\pm 0.2) \times 10^5 \exp(-71\ \text{kJ mol}^{-1}/RT)\ \text{s}^{-1}$.

Introduction

The main oxidizing species produced in the γ-radiolysis of water are the OH radical and molecular H_2O_2, and a complete understanding of their kinetics is important for many aspects of fundamental and applied radiation effects.[1−3] It is usually assumed that the primary mechanism to form H_2O_2 is the fast combination reaction of OH radicals. These reactions occur in the initial nonhomogeneous distribution of water decomposition products, commonly called a spur, produced by the deposition of energy by the γ-ray. No real-time studies on H_2O_2 formation have been performed so its temporal dependence is usually probed by varying the concentration of selective scavengers for the OH radical.[4−7] These scavenging experiments have suggested that the sole precursor to H_2O_2 formation is the OH radical and the studies have provided information on the diffusion-kinetics of spurs at room temperature. Irradiation of water at high temperatures leads to a decrease in H_2O_2 yields due to an increase in the rate of relaxation of the spur. The yields of H_2O_2 have been determined at high temperatures only in the low scavenger concentration regime.[8−10] The corresponding time is on the order of microseconds and the yields, known as escape yields, represent the limiting value following the complete relaxation of the spurs to a homogeneous distribution of water products. The time scale for the formation of H_2O_2 has not been determined at elevated temperatures. In this work, selective OH radical scavengers are used to probe the time dependence of the formation of H_2O_2 at temperatures up to 150 °C. The results give fundamental information on the diffusion-kinetics of the main oxidizing species in the γ-radiolysis of water at elevated temperatures.

An important practical application for examining the radiolytic formation of H_2O_2 at elevated temperatures is its role in nuclear power reactors. Hydrogen peroxide formed in the radiolysis of water is found to be the main corrosion product, and it is involved in oxidation damage in almost every domain of nuclear technology.[11] For instance, hydrogen peroxide has been found in the core and in the recirculation lines of boiling water reactor (BWR) plants. A major problem in the assessment of H_2O_2 damage in the steady-state operation of BWRs is that it undergoes thermal decomposition at higher temperatures. It is also very difficult to measure radiation chemical yields directly in the harsh environments of reactor cores. Therefore, reliable measurements on the yields and kinetics of H_2O_2 in the radiolysis of water give extremely useful data for reactor design and management.

It this work, the production of H_2O_2 was examined in the γ-radiolysis of water at elevated temperatures. Methanol, ethanol, and bromide were used as scavengers of the OH radicals to give the temporal dependence of H_2O_2 formation. Temperatures were varied from 25 to 150 °C. Information was also obtained on the thermal decomposition rate of H_2O_2 at temperatures above 100 °C.

Experimental Section

The steady-state experiments were carried out using three different ^{60}Co γ-sources at the Radiation Laboratory of the University of Notre Dame. Dose rates were 1.1, 3.9, and 19 krad/min as determined by Fricke dosimetry.[4,7] All solutions were freshly prepared before each experiment with water purified by a Millipore Milli-Q UV system. Methanol, ethanol, and NaBr were of the highest grade commercially available. Hydrogen peroxide was determined by the Ghormley tri-iodide method with KI, in which iodide is oxidized to I_3^- by the hydrogen peroxide.[7,12,13] Absorption measurements of I_3^- were done at its peak maximum, λ_{max}, taking into account that λ_{max} shifts with solvent composition. The absorbance of the dilute aqueous solutions was measured at 350 nm using a diode array spectrophotometer (Hewlett-Packard HP8453). The molar extinction coefficient of I_3^- at 350 nm, ϵ_{350}, was calibrated by a standard solution of H_2O_2 (Fischer Scientific) and was found

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to be 25500 M^{-1} cm^{-1}. The equilibrium constant for $I^- + I_2 \Leftrightarrow I_3^-$ was found to be 800 M^{-1}. To keep the equilibrium quantitatively on the side of I_3^- the concentration of iodide was kept at 0.12 M. For the solutions with high solute concentrations the previously determined ϵ_{350} value of 26000 M^{-1} cm^{-1} was used.[7] All solutions contained 25 mM $NaNO_3$ to inhibit destruction of the H_2O_2 by hydrated electrons and H atoms. The only exception was the lowest (10^{-5} M) concentration of methanol, which was 2.5 mM in $NaNO_3$ to minimize cooperative effects, see below.

Radiolysis at elevated temperatures was performed using a specially designed oven that fits in the sample drawers of the cobalt sources. The oven consisted of a 25.4 mm diameter brass cylinder, 102 mm long, and with caps on each end. It was insulated with a 25.4 mm ID, 50.8 mm OD, cylinder of alumina−silica. The brass cylinder was bored axially to 10 mm to accept a Pyrex sample cell. Each of the end caps contained a 100-watt cartridge heater and temperature was maintained to within 2% with an Omega Engineering temperature controller. Examination of the cylinder with thermocouples showed that a uniform temperature was maintained throughout the cylinder interior after equilibrium was achieved, which took about 30 min. The main advantage of the oven design is that a sample cell can be inserted and reach equilibrium within a few minutes and then be quickly retrieved and cooled. The sample cells were made from 10 mm OD Pyrex tubes sealed on one end and with a slight restriction near to the other open end. Prior to irradiation the sample cells were sealed with rubber septa, purged with helium, and permanently sealed by heating and drawing the tube closed at the restriction. Each sample cell contained about 5 mL of solution. Removing the cells from the source immediately after irradiation and immersing them in cold water minimized thermal decomposition of the H_2O_2.

Error limits for H_2O_2 yields are estimated to be about ±2% for small scavenger concentrations and about ±4% for high scavenger concentrations because of the small yields measured.

Results and Discussion

The γ-radiolysis of water leads to a series of isolated spurs consisting of nonhomogeneous distributions of water decomposition products.[1−3] The main oxidizing species is the OH radical produced by proton transfer from the molecular water cation to a neighbor water molecule.[14] To a lesser extent O atoms are also produced, and in γ-radiolysis they react immediately with water to give two OH radicals. Other reactive species also produced in water radiolysis are e_{aq}^- and H atom. All permutations of radical reactions are possible, but the predominant reactions of the OH radicals as the nonhomogeneous distributions relax by diffusion are the following:

$$\bullet OH + \bullet OH \rightarrow H_2O_2 \quad 2k_1 = 1.1 \times 10^{10}\ M^{-1}\ s^{-1} \tag{1}$$

$$\bullet OH + e_{aq}^- \rightarrow OH^- \quad k_2 = 3.0 \times 10^{10}\ M^{-1}\ s^{-1} \tag{2}$$

All room-temperature rate constants used here were taken from Buxton et al.[15] It has been shown that the temporal dependence of H_2O_2 formation can be obtained by selective scavenging of the OH radical.[16] This procedure provides an easy method to obtain temporal dependences of water products using end product analysis.

The OH radical scavengers used here are methanol, ethanol, and bromide. All are efficient OH scavengers without producing undesirable side effects.

$$\bullet OH + CH_3OH \rightarrow \bullet CH_2OH + H_2O \qquad k_{3a} = 9.7 \times 10^{8}\ M^{-1}\ s^{-1} \tag{3a}$$

$$\bullet OH + C_2H_5OH \rightarrow CH_3C\bullet HOH + H_2O \qquad k_{3b} = 1.9 \times 10^{9}\ M^{-1}\ s^{-1} \tag{3b}$$

$$\bullet OH + Br^- \rightarrow \bullet BrOH^- \quad k_{3c} = 1.1 \times 10^{10}\ M^{-1}\ s^{-1} \tag{3c}$$

The scavenging capacity of the system is defined as the product of the scavenger concentration and the appropriate rate constant. The scavenging capacity is formally equivalent to the pseudo-first-order rate constant and its inverse gives the lifetime for the formation of H_2O_2 in neat water. As discussed below, there are other more sophisticated methods using Laplace transform techniques by which the scavenging capacity dependence of H_2O_2 yields can give accurate temporal dependences.[16]

Hydrogen peroxide is determined in this study as an end product. It therefore must be protected from the e_{aq}^- and H atoms escaping the spurs. At long times the following reactions will considerably lower the observed H_2O_2 yields unless they are prevented from occurring:

$$e_{aq}^- + H_2O_2 \rightarrow \bullet OH + OH^- \quad k_4 = 1.1 \times 10^{10}\ M^{-1}\ s^{-1} \tag{4}$$

$$\bullet H + H_2O_2 \rightarrow \bullet OH + H_2O \quad k_5 = 9.0 \times 10^{7}\ M^{-1}\ s^{-1} \tag{5}$$

In all of the experiments reported here, sodium nitrate was added to scavenge hydrated electrons and hydrogen atoms.

$$e_{aq}^- + NO_3^- \rightarrow NO_3^{2-} \quad k_7 = 9.7 \times 10^{9}\ M^{-1}\ s^{-1} \tag{6}$$

$$H + NO_3^- \rightarrow HNO_3^- \quad k_8 = 1.4 \times 10^{6}\ M^{-1}\ s^{-1} \tag{7}$$

The concentration of sodium nitrate was 25 mM in all solutions except one. At the higher solute concentrations this amount of nitrate ensures that it will react with essentially all the hydrated electrons and H atoms before they undergo any significant reaction with hydrogen peroxide. At the lowest methanol concentration (10^{-5} M) 25 mM of nitrate can scavenge the hydrated electron before the alcohol scavenges the OH radical. Since one of the major reaction of the hydrated electron is with the OH radicals (reaction 2) scavenging it too soon will lead to an increase in OH yields above that expected. Therefore, at the lowest methanol concentration (10^{-5} M) the nitrate was 2.5 mM in order not to interfere with the normal OH radical chemistry in the spur. Previous work has shown that the increase in OH radical yields is only about 5% over these nitrate concentrations.[5,6] Extensive studies examining the cooperative effect of nitrate/methanol solutions on H_2O_2 formation are underway.

The dependence of H_2O_2 formation on scavenger concentration in the γ-radiolysis of water was first performed at room temperature using a number of different scavengers. The purpose of these experiments was to match previous data in order to reveal any discrepancies and to verify that the scavenger systems were clear of any undesirable side effects. Some scavengers can produce secondary products that interfere in the normal water chemistry, especially when they are added at high concentrations. Figure 1 shows the results at room temperature and a dose rate of 1.06 krad/min for the yields of H_2O_2 as a function of the scavenging capacity of the system. This figure

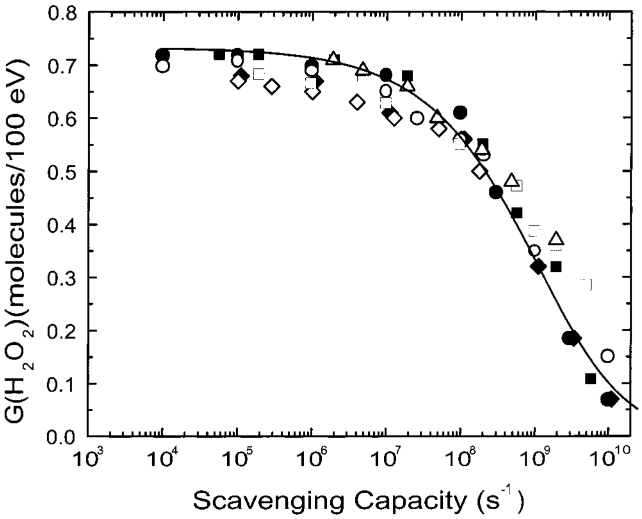

Figure 1. Hydrogen peroxide yields in γ-radiolysis as a function of the scavenging capacity for •OH radicals: (●) methanol and 25 mM sodium nitrate, this work; (■) ethanol and 25 mM sodium nitrate, this work; (◆) bromide and 25 mM sodium nitrate, this work; (◇) aerated bromide, ref 4; (○) methanol and 25 mM sodium nitrate, ref 7; (□) ethanol and acetone, ref 5; (△) ethanol and sodium nitrate, ref 6. The solid line is from eqs I and II using the parameters of Table 1 for methanol at 25 °C.

contains the results of the present work for methanol, ethanol, and bromide, as well as previous results at neutral pH using these same scavengers.[4−7] The results throughout this work are presented in terms of the radiation chemical yields with units of molecules/100 eV of total energy absorbed by the entire system (water and scavenger). It can be seen that the general agreement between the results is very good. The unique scavenging capacity dependence indicates that the scavenger systems perform as expected. Some discrepancy between the present results and that from the literature can be seen at very high concentration of scavengers where the present yields are distinctively lower. This difference is probably due to impurities in the solutes used in the previous work. At high scavenger concentrations these impurities make up a significant fraction of the total system. It was found that using less than the best quality methanol and ethanol available leads to increased H_2O_2 yields at the highest alcohol concentrations.

The yield of hydrogen peroxide at high scavenging capacities is very small and difficult to measure. However, the relatively higher yields in previous studies could be interpreted as due to a unimolecular source of H_2O_2. The trend with the present results and the yield of only 0.07 molecules/100 eV at a scavenging capacity of about 10^{10} s^{-1} strongly suggests that the limiting G (H_2O_2) value at high scavenger capacity is zero. Hydrogen peroxide production in γ-radiolysis at times less than ~1 μs is due almost exclusively to spur reactions of the OH radicals.

Low scavenger concentrations correspond to long times, and the limiting yield represents the amount of product that escapes into the bulk following the relaxation of the spur by diffusive processes. At times longer than a few microseconds the distribution of water decomposition products in γ-radiolysis is essentially homogeneous. The escape yield represents the yield found in continuous or long-time radiolysis conditions, which is of significant practical importance. All the scavengers used in this work give similar escape yields, G_{esc} (H_2O_2) $= 0.73 \pm 0.02$ for methanol, 0.74 ± 0.02 for ethanol, and 0.70 ± 0.02 for bromide. The results agree nicely with previous results which establish the escape yields of hydrogen peroxide with γ-rays to be 0.70 ± 0.03 molecules/100 eV.[7] Experiments also show that the G value is constant with dose up to about 100 krad suggesting that possible side effects due to the reactions of nitrate or products from the scavenging reactions are negligible.

TABLE 1: Parameters for the Model Fit to the Scavenger Data

scavenger	temperature °C	G_{esc} molecules/100 eV	α ns
methanol	25	0.733	0.721
	60	0.668	0.642
	80	0.605	0.616
	100	0.551	0.883
	120	0.494	0.875
	150	0.429	0.562
ethanol	25	0.737	0.569
bromide	25	0.701	0.606
	100	0.488	0.706
	120	0.439	0.405
	150	0.408	0.277

It is sometimes important in many practical applications to be able to predict H_2O_2 yields at a particular scavenging capacity of the OH radical. Fundamental radiation chemistry studies often require the time dependence of product formation in order to compare with model calculation. Extensive studies on the diffusion-kinetics within a spur suggest that the scavenger capacity dependence of H_2O_2 yields can be well characterized using the following empirical relationship:[16]

$$G_s\,(H_2O_2) = G_{esc}\,(1 - F(s)) \qquad \text{(I)}$$

$$F(s) = ((\alpha s)^{1/2} + (\alpha s)/2)/(1 + (\alpha s)^{1/2} + (\alpha s)/2) \qquad \text{(II)}$$

Here, G_{esc} is the long time or escape yield, s is the scavenging capacity of the system, and α is a time constant. Another parameter representing the initial yield, G_o, is usually included in eq I, but it is assumed to be zero in the case of H_2O_2. The value of α depends on the reactant (OH radical in this work) and the type of radiation (γ-rays in this work). The data of the present work were fit using nonlinear least-squares methodology to eqs I and II to give the results given in Table 1. The solid line in Figure 1 shows the predicted yields using eqs I and II with the constants for methanol at 25 °C. The form of eq II was chosen because it well represents the track kinetics expected for γ-rays and because an analytical form of its inverse Laplace transform exists.[16] The temporal dependence of H_2O_2 can be obtained readily from an equation similar to that for the scavenging capacity dependence using the same data parametrization values.

$$G_t\,(H_2O_2) = G_{esc}\,(1- F(t)) \qquad \text{(III)}$$

$$F(t) = 2F_f\,((4.0t/(\alpha\pi))^{1/2}) \qquad \text{(IV)}$$

The auxiliary function for the Fresnel integrals, F_f, can be easily evaluated using standard algorithms.[17] Inverse Laplace transforms can be problematical because they require a large (infinite) amount of data. The use of an analytic formula greatly simplifies data analysis without sacrificing precision.

All the experiments presented in Figure 1 were performed at a relatively low dose rate of 1.06 krad/min to minimize radical−radical termination reactions in the spur, which could affect the escape yield. The effect is not expected to be significant with primary radical reactions in the spur, but secondary reactions due to the added solutes could cause problems. Secondary reactions may especially be significant at higher temperatures. Therefore, the effect of dose rate on the escape yield of hydrogen peroxide has been measured with methanol and bromide as

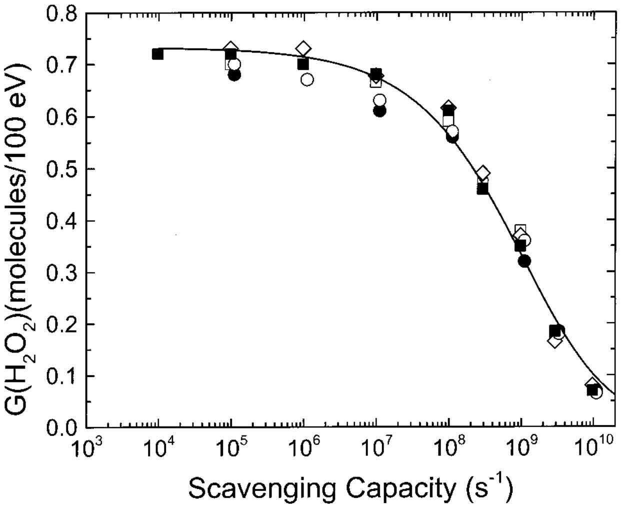

Figure 2. Hydrogen peroxide yields as a function of the scavenging capacity of methanol and bromide at different dose rates. All solutions deaerated with methanol or bromide and 25 mM sodium nitrate, pH neutral: (■) methanol at 1.06 krad/min; (□) methanol at 3.79 krad/min; (◇) methanol at 19.03 krad/min; (●) bromide at 1.06 krad/min; (○) bromide at 19.03 krad/min. The solid line is the same as in Figure 1.

scavengers at the higher dose rates of 3.79 and 19.03 krad/min. Other conditions of the system remain the same as in Figure 1, i.e., deaerated and neutral pH aqueous solutions containing 25 mM $NaNO_3$ and different concentrations of scavengers. Figure 2 shows the yields of H_2O_2 as a function of scavenging capacity of methanol and bromide for the three different dose rates. It can be seen that variation in the dose rate by a factor of 20 does not influence the escape yield of hydrogen peroxide, irrespective of the type of scavenger. Sunaryo et al. examined the products of the scavenging reactions and came to similar conclusions that secondary reactions were not significant in methanol solutions at high temperature.[18] The products of the scavenging reactions probably react with themselves or with water to form stable products that do not decompose hydrogen peroxide.

The scavenging capacity dependence of hydrogen peroxide at elevated temperatures gives valuable new information on the chemistry in spurs. Figure 3 shows the yields of hydrogen peroxide as a function of the scavenging capacity of methanol at 25, 60, 80, 100, 120, and 150 °C. The scavenging capacity was calculated taking into account the changes in the density of water with increasing temperature.[19] For mixtures with high methanol concentration the density is calculated assuming the additivity of the different components, e.g., at the highest methanol concentration the alcohol is 20 wt % of the solution. The rate coefficients for the reaction of methanol and the hydroxyl radical (reaction 3a) have been calculated by using the activation energy of 4.8 kJ mol^{-1}, and the resulting rate coefficients are expected to have errors of <10%.[20] Such small errors are not noticeable on the logarithmic scavenger capacity scales used here. With increasing temperature the plateaus or escape yields at low scavenger concentrations decrease. It appears that the inflection points of the curves remain unchanged with increasing temperature at a value of about 10^9 s^{-1}. The limiting yields at the highest scavenging capacities are nearly independent of temperature and appear to approach zero. This result suggests that the OH radical is the precursor to hydrogen peroxide at all temperatures.

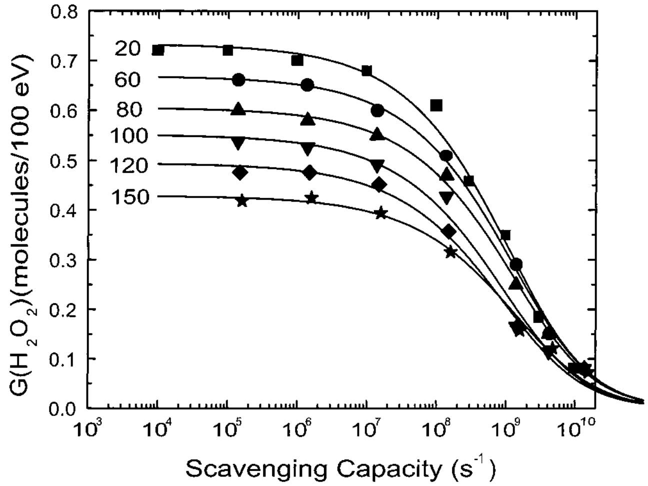

Figure 3. Hydrogen peroxide yields as a function of the scavenging capacity of methanol (25 mM nitrate, deaerated, pH neutral) at different temperatures: (■) 25 °C; (●) 60 °C; (▲) 80 °C; (▼) 100 °C; (◆) 120 °C; (★) 150 °C. The solid lines are from eqs I and II using the parameters of Table 1 for methanol.

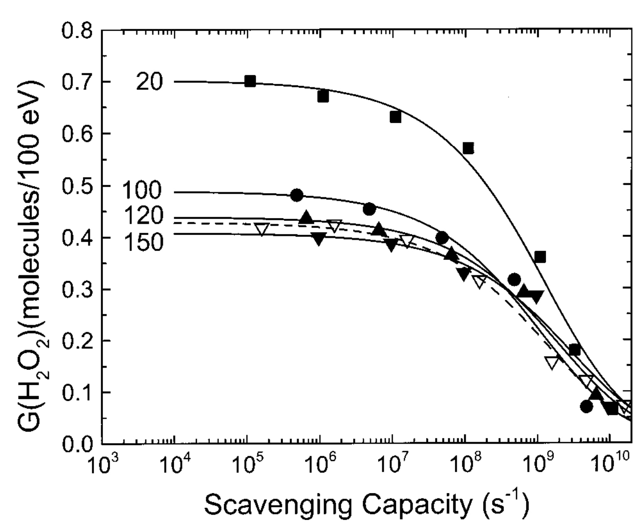

Figure 4. Hydrogen peroxide yields as a function of the scavenging capacity of bromide (25 mM nitrate, deaerated, pH neutral) at different temperatures: (■) 25 °C; (●) 100 °C; (▲) 120 °C; (▼) 150 °C; (▽) methanol at 150 °C. The solid lines are from eqs I and II using the parameters of Table 1 for bromide and the dashed line is for methanol at 150 °C.

High temperatures could cause unknown, adverse effects on the methanol and can lead to false radiation chemical yields of H_2O_2. For instance, methanol could thermally decompose at high temperature to give undesirable products that interfere with the chemistry or there could be a significant change in methanol concentration. Previous results suggest that aqueous methanol solutions are stable to about 450 °C,[21] but it was decided to confirm this observation with the present experimental configuration. Additional experiments were performed using a bromide as a scavenger with the other conditions unchanged from the methanol solutions. The scavenging capacity for the hydroxyl radical with bromide has been calculated on the same way as for methanol. The activation energy of 18 kJ mol^{-1} for the reaction between bromide and the OH radical has been used.[20] Figure 4 shows the yield of hydrogen peroxide as a function of scavenging capacity of bromide at 25, 100, 120, and 150 °C. Comparison between the results using the two scavengers shows that the plateaus or low scavenger limiting yields with bromide are slightly lower than for methanol at the high temperatures. However, the differences are within the experimental errors. The results for methanol at 150 °C are given in Figure 4 for

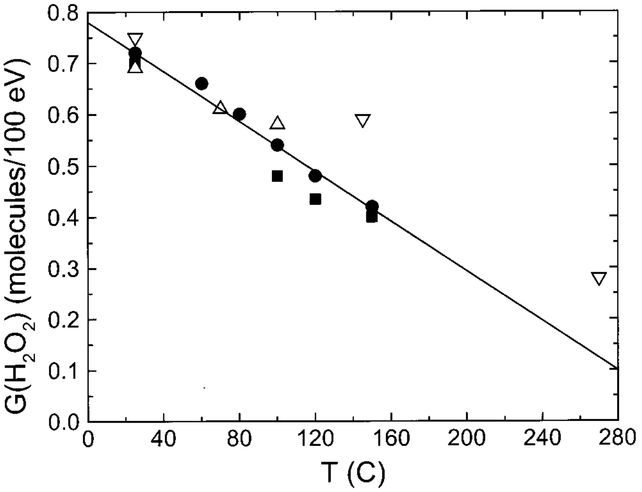

Figure 5. Limiting hydrogen peroxide yields at low scavenger concentration as a function of temperature: (● methanol, this work; (■) bromide, this work, (△) acrylamide, ref 9; (▽) iodide and N_2O, ref 10. The solid line is a linear fit through the methanol data.

comparison. To minimize the thermal decomposition of hydrogen peroxide all data presented in Figures 3 and 4 were made at a dose rate of 19.6 krad/min. This dose rate used the least amount of time and the reported *G* values were obtained by extrapolating to zero dose. Dose rate effects will be discussed below.

Two other groups investigated the temperature dependence of H_2O_2 production in γ-radiolysis at low scavenger capacities. Elliot et al. measured hydrogen peroxide yields in light and heavy water using 0.5 mM acrylamide as a scavenger to prevent the primary radicals from destroying the peroxide.[9] They also used the Ghormley tri-iodide method with a dose range of 3−12 krad. Their *G* values extrapolated to zero dose at 20, 70, and 100 °C are 0.69 ± 0.02, 0.61 ± 0.04, and 0.58 ± 0.03 molecules/100 eV, respectively. The correlation between the temperature and the *G* value can be given by $G\ (H_2O_2) = 0.72 - 1.40 \times 10^{-3}$ T (°C). Kent and Sims measured the yield of H_2O_2 over the temperature range 25−270 °C in a high temperature and high pressure loop by measuring the oxygen production. They used slightly alkaline solutions containing iodide ions as scavengers and saturated with N_2O.[10] The reported *G* values for H_2O_2 at 25, 145, and 270 °C are 0.75, 0.59, and 0.28 molecules/100 eV, respectively. From these results the correlation between the temperature and the *G* value can be given by $G\ (H_2O_2) = 0.82 - 1.92 \times 10^{-3}$ T (°C). The low scavenging capacity limiting yields for hydrogen peroxide measured in this work are shown in Figure 5 with the results of the above data. The correlation between the temperature and the *G* value for methanol in the present work has been calculated to be $G\ (H_2O_2) = 0.78 - 2.43 \times 10^{-3}$ T (°C), which is shown as a solid line in Figure 5. For bromide this correlation was found to be $G\ (H_2O_2) = 0.74 - 2.40 \times 10^{-3}$ T (°C). For both of the scavengers examined here, these correlations give larger negative slopes than those from Elliot et al.[9] and Kent and Sims,[10] i.e., the yield of hydrogen peroxide in the present work decreases faster with increasing temperature. The main discrepancy with Elliot et al. is with the datum at the highest temperature, while the other data agree well. Kent and Sims used N_2O saturated solutions, which converts hydrated electrons to OH radicals, thereby making a direct comparison between the results improper.

The H_2O_2 yield has been measured at temperatures of 25, 60, 80, 100, 120, and 150 °C with methanol as a scavenger and at 25, 100, 120, and 150 °C for bromide scavenger. Because of the fast decomposition of H_2O_2, it was impossible to measure its yield at higher temperature using the present experimental configuration. Hydrogen peroxide thermally decomposes to give two OH radicals.

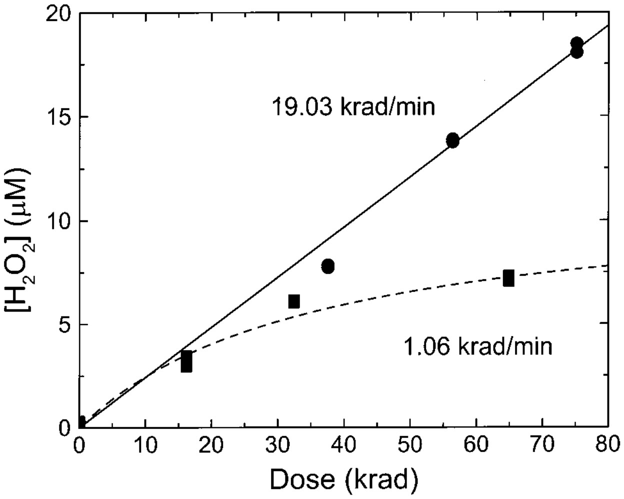

Figure 6. Concentration of hydrogen peroxide as a function of dose for deaerated aqueous solutions of 1 mM methanol and 25 mM sodium nitrate, pH neutral, at 120 °C: (■) 1.06 krad/min; (●) 19.03 krad/min.

$$H_2O_2 \rightarrow \bullet OH + \bullet OH \qquad (8)$$

Takagi and Ishigure find the activation energy of reaction 8 to be 71 kJ mol^{-1} with a rate coefficient of $k_8 = 6.4 \times 10^5 \exp(-71\ \text{kJ mol}^{-1}/RT)\ \text{s}^{-1}$.[22] Thus, the thermal decomposition half-life, $\tau_{1/2} = \ln(2)/k_8$, of H_2O_2 can be estimated to be 158, 49, and 11 min at 100, 120, and 150 °C, respectively. At 200 °C its half-life is only 77 s, which makes it difficult to perform normal radiation chemical studies using end product analysis.

It was previously mentioned that the results presented here in Figures 3 and 4 were obtained at the highest dose rate available to prevent errors caused by the thermal decomposition of hydrogen peroxide during the irradiation. Additional experiments at lower dose rates showed no measurable changes in yields of hydrogen peroxides. However, because of its thermal decomposition, the dependence of the H_2O_2 concentration on dose deviated significantly from linearity at low dose rates with temperatures above 100 °C. The relatively longer irradiation time leads to a greater destruction of H_2O_2. Figure 6 shows the dose dependence for H_2O_2 concentration using methanol as a scavenger irradiated at 1.06 and 19.06 krad/min and a temperature of 120 °C. At the higher dose rate it takes only a couple of minutes to reach a dose of 60 krad and the dose response is linear. At the lower dose rate it takes a much longer irradiation time to reach the same dose, and the thermal decomposition of H_2O_2 is now significant. The difference in the dose response can be used to measure the thermal decomposition half-life of hydrogen peroxide at the higher temperatures using the following equation:

$$k_{\text{obs}} = k_D \exp(-E_a\ \text{kJ mol}^{-1}/RT)\ \text{s}^{-1}$$

where $k_{\text{obs}} = \ln 2/\tau_{1/2}$, k_D is the preexponential factor, and E_a is the activation energy. Using the activation energy of 71 kJ mol^{-1}, the estimated lifetimes for the thermal decomposition of H_2O_2 at 100, 120, and 150 °C are 145, 47, and 9 min, respectively, which are very close to those values of Takagi and Ishigure.[22] The calculated rate coefficient for the thermal decomposition of hydrogen peroxide is estimated to be 6.5 (±0.2) $\times 10^5 \exp(-71$ kJ mol$^{-1}/RT)$ s^{-1}.

A recent paper by Croiset et al. reported an activation energy of 182 kJ mol^{-1} for the decomposition of H_2O_2 in supercritical water and 46 kJ mol^{-1} for water in the range of 150−450 °C.[22] Their reported rate coefficient for the thermal decomposition of H_2O_2 in the lower temperature regime is $10^{3.5\pm0.2} \exp(-46$ kJ mol$^{-1}/RT)$ s^{-1}. Half-life values estimated from this equation are 10, 5, and 2 min for 100, 120, and 150 °C, respectively. These values are considerably lower than those of Takagi and Ishigure[22] and the present results. The observed differences may be due to wall effects. The present work used Pyrex cells, while Takagi and Ishigure[22] and Croiset et al.[23] used stainless steel and Inconel reactors, respectively. Further experiments examining the thermal decomposition of hydrogen peroxide are in progress.

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