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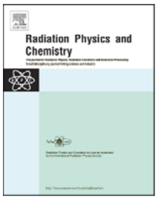

The effect of interfacial mass transfer on steady-state water radiolysis

Pamela A. Yakabuskie, Jiju M. Joseph, J. Clara Wren*

Department of Chemistry, The University of Western Ontario, London, Ontario, Canada N6A 5B7

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The effect of aqueous–gas interfacial transfer of volatile species on the γ-radiolysis of water was studied as a function of gas-to-liquid volume ratio at various solution pHs and cover gas compositions. Water samples with cover-gas headspace were irradiated at an absorbed dose rate of 2.5 Gy s^{-1} and the radiolytic productions of H_2 in the cover gas and H_2O_2 in the water phase were monitored as a function of irradiation time. The experimental results were compared with computer simulations using a water radiolysis kinetics model that included primary radiolysis, subsequent reactions of the primary radiolysis products in the aqueous phase, and aqueous–gas interfacial transfer of the volatile species H_2 and O_2. This study shows that the impact of the interfacial mass transfer strongly depends on pH. At pH ≤ 8 (lower than the pKa of •H of 9.6) the effect of aqueous-to-gas phase transfer of the volatile species on the steady-state concentrations of the other radiolysis products is negligible. At higher pHs (≥ 8), radiolytic production of O_2 is slow but considerable, which results in significant increase in the steady-state concentrations of H_2 and H_2O_2 compared to those at lower pHs. Thus, in the presence of headspace, the interfacial transfer of both H_2 and O_2 becomes significant, and the aqueous concentrations of H_2 and O_2 are no longer independent of the interfacial surface area and water volume. Nevertheless, the accumulated mass of H_2(g) in the headspace is proportional to the aqueous concentration of H_2 at all pHs, and the gaseous concentration of H_2 in the headspace can be used to infer the aqueous concentration of H_2.

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1. Introduction

Accurate understanding of the effects of ionizing radiation on nuclear reactor system chemistry and materials performance is important for assessment of various operational and maintenance requirements and safety margins of nuclear power plants. Of particular concern is the chemistry driven by the radiolysis of water. Deposition of ionizing radiation into water leads to the formation of primary water radiolysis products as given in R1

$$H_2O \xrightarrow{rad} \bullet OH, \bullet e^-_{aq},\ \bullet H,\ HO_2\bullet, H_2, H_2O_2, H^+ \qquad (R1)$$

The primary water decomposition products differ considerably in their chemical reactivity and redox property. They can participate in electrochemical reactions leading to corrosion, and understanding their production rates and subsequent reactions can provide the basis for selecting materials and water chemistry control agents to mitigate corrosion.

The most studied parameter for radiolysis of a solution (typically water with an additive) has been the primary radiolysis yield, often expressed using *G*-values in units of number of species formed per 100 eV of absorbed energy. These are the product yields when the products reach homogeneous distribution along the radiation track, and are typically obtained in a 10–100 ns time scale following deposition of finite (short term) pulse radiation energy. The primary radiolysis products, once generated, undergo further chemical reactions with each other, water molecules and any other chemical species in solution, and the solution chemistry changes with time. This longer-term stage (> 100 ns) is often referred to as the chemistry stage. The reactions of the primary radiolysis products in the chemistry stage can be described by classical chemical reaction rate and transport equations as a function of macroscopic properties such as concentration, temperature, or thermodynamic state properties of the solution.

The elementary reactions of the primary radiolysis products with each other and other water-derived species have been studied extensively, and pulse radiolysis studies have been extremely useful for establishing the primary radiolysis yields and the rates of these fast free radical and ion reactions (Allen, 1961; Draganic and Draganic, 1971; Farhataziz and Rodgers, 1987; Spinks and Woods, 1990; Buxton et al., 1988). These studies have established that, when radiation of a solution ceases and direct radiolytic production of primary radiolysis products stops, the reactive species quickly form stable molecular products, H_2, O_2, H_2O_2, and H_2O. However, under long-term irradiation, the solution chemistry evolves towards a steady state

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* Corresponding author: Tel.: 1 519 661 2111 x 86339; fax: 1 519 661 3022.
E-mail address: jcwren@uwo.ca (J. Clara Wren).

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(or pseudo-steady state) in which the concentrations of radiolysis products differ substantially from the concentrations associated with the primary radiolysis yields or the final molecular products. The steady-state concentration of a radiolysis product will depend on its radiolysis production rate and chemical decomposition rate, where the radiolysis production rate is constant at a constant dose rate, but the decomposition rate increases as the species concentration increases with irradiation time. The chemical decomposition rates are very sensitive to aqueous environments such as pH, temperature and chemical additives. Thus, while chemical additives such as pH- or redox-controlling agents at low concentrations will not significantly affect the primary radiolysis yields (Spinks and Woods, 1990), they can significantly affect the subsequent chemical reactions leading to steady-state species concentrations. For example, the concentrations of H_2 and H_2O_2 are more than two orders of magnitude greater in water with a pH of 10.6 compared to water with a pH of 6.0 following an extended period of γ-radiolysis (Joseph et al., 2008).

For most situations of practical interest, radiation fields are present on a continuous basis, or at least over time scales that are long compared to the time scale for primary radiolysis species production. Most corrosion processes (oxidation/dissolution), or other processes involving interfacial reactions and transport, have high activation energies and only occur substantially over long time periods. Hence, constant radiation fields will drive water radiolysis chemistry that can influence the corrosion of reactor structural materials over those time scales. To assess these impacts of long-term radiolysis on corrosion requires that we understand and can predict the speciation and concentrations in water under steady-state conditions. Despite the importance of radiation-induced processes in a constant radiation field, studies on steady-state water radiolysis are sparse (Hochanadel, 1952, Boyd et al., 1980, Driver et al., 2000, Wren and Glowa, 2000; Joseph et al., 2008). This study adds to our understanding of steady-state water radiolysis and, in particular, our ability to accurately model important species that are used for redox chemistry control in nuclear systems.

Water radiolysis produces two volatile species, H_2 and O_2. In the presence of headspace or cover gas volume, these species can transfer to the gas phase until equilibrium is established (or O_2 may transfer from the gas phase to the liquid phase when air is introduced into a cover gas). The impact of this aqueous–gas interfacial mass transfer on radiolysis driven chemistry has not been studied systematically. This is important because it can impact on predictions of hydrogen gas generation (particularly if the headspace communicates with other gas volumes). Volumes of hydrogen in the gas phase are important because they represent a potential combustion hazard. Interfacial transfer of volatile species can also alter the aqueous phase concentrations, and because of the complex chemistry, affect the steady-state concentrations of the reactive species that are most important in controlling corrosion rates. Quantitative understanding of interfacial mass transfer and its connection to the aqueous state has another important application. Measurement of the amount of H_2 and O_2 in a gas sample is much simpler and more accurate than measurement of the quantities of these species dissolved in water (no gas stripping of water samples is required). Under many extreme experimental conditions and frequently for in-plant system chemistry monitoring, cover-gas analysis may be the only practical measurement that can be carried out.

This study examines the effect of interfacial transfer of the volatile radiolysis products H_2 and O_2 on steady-state water radiolysis chemistry by performing experiments and analyzing their results using a water radiolysis chemical kinetics model that includes the aqueous–gas phase transfer kinetics of the volatile species.

2. Experimental

All experiments were performed with water purified to a resistivity of 18.2 MΩ cm using a NANOpure Diamond UV ultrapure water system from Barnstead International. The experiments at pH 6.0 were performed without the addition of any buffer and those performed at pH 10.6 used a phosphate buffer (10^{-3} mol dm^{-3}). The pH of the solution was measured prior to, and at the end of, the irradiation period using a pH meter (Accumet). The samples were irradiated in glass vials (20 ml) that were capped using aluminum crimp caps with PTFE silicone septa (Agilent Technologies) to provide a vacuum tight seal so as to ensure no loss of gaseous species. The de-oxygenated water samples were prepared by purging a bulk solution with ultra high purity argon (impurity $<0.001\%$), for more than 1 h. The solution was then transferred into glass vials and the vials were sealed inside an Ar-purged glove box where the oxygen concentration was maintained below 1000 ppm. For aerated samples, a bulk solution was saturated with hydrocarbon free air (Praxair) for more than 1 h and individual vials were saturated for 10 min and capped, before the solution was transferred into the vials with a syringe. The experiments were performed with different ratios of gas volume to aqueous volume, V_g/V_{aq}, in the vials with the aqueous–gas interfacial area constant at 3.14 cm^2 (the cross-sectional area of the vials).

Irradiation was carried out in a ^{60}Co gamma cell (MDS Nordion), which provided the irradiation chamber with a uniform absorption dose rate of 2.5 Gy s^{-1} determined using Fricke dosimetry (Spinks and Woods, 1990; Upadhyay et al., 2002). The vials were held in a specially designed sample holder so as to have a reproducible uniform dose distribution during irradiation. Individual vials were taken out of the gamma cell at regular time intervals and the gas was sampled and analyzed for H_2 and the liquid was sampled and analyzed for H_2O_2.

The concentration of hydrogen peroxide was determined by the Ghormley tri-iodide method (Hochanadel, 1952) in which I^- is oxidized to I_3^- by H_2O_2 in the presence of ammonium molybdate catalyst. The I_3^- concentration was measured using UV spectrophotometry of the I_3^- absorption at 350 nm with a molar extinction coefficient of 25 500 M^{-1} cm^{-1} (Stefanic and LaVerne, 2002). Using this method, the detection limit for $[H_2O_2]$ was 3×10^{-6} mol dm^{-3} and the uncertainties in the measurement arising from sampling and instrumental errors were estimated to be $\pm0.2\%$ at the lower end of the measured concentration range and $\pm0.05\%$ at the higher end of the measured range. The H_2O_2 analysis was performed immediately after removal of a vial from the gamma cell to minimize any thermal decomposition of H_2O_2 in the sample vials.

The gas sampling was carried out using a gas-tight syringe with a luer lock valve (Agilent Technologies) and gas samples were injected into the GC through a gas-sampling valve and septum into the sample loop. The GS-GASPRO column used is connected to three detectors; Thermal Conductivity Detector (TCD), μ-Electron Capture Detector (μ-ECD) and Mass Selective Detector (MSD) as described in detail in a previous paper (Joseph et al., 2008). Quantification of the amount of H_2 in the cover gas was performed using a TCD detector and nitrogen is used as the carrier gas at a flow rate of 4.6 ml/min. Using this method, the detection limit for the gaseous concentration $[H_2(g)]$ was 1.0×10^{-5} mol dm^{-3} and the uncertainties in the measurement arising from sampling and instrumental errors were estimated to be $\pm50\%$ at the low end of the measured concentration range and $\pm0.005\%$ at the high end of the concentration range.

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