

Kinetic analysis of hydrogen and hydrogen peroxide by ammonia radiolysis

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1. Introduction

Ammonia is used in VVER (Water-Water Energy Reactor) reactors of Russian design for control of dissolved oxygen concentration. On the other hand, in western Pressurized Water Reactors (PWRs) hydrogen is added to the system to scavenge oxygen through radiation induced reactions. In the case of NH₃, it has been proposed that in the reactor its radiolysis leads to the formation of hydrogen, which then combines with oxygen. However, at parts per million (ppm) concentrations of ammonia, production of hydrogen by direct effect of radiolysis is not possible. As compared to pure water, in dilute ammonia solutions the G-value for H₂ can increase and approach the molecular yield value of 0.45, but this increase will happen in the case of any other reactive solute capable of reacting with OH radicals. This approach, however, does not explain the formation of nitrite as a product of radiolysis in aerated aqueous solutions of ammonia. The formation of NO₂⁻ indicates that ammonia reacts with oxygen in some way. The radiolysis of NH₃ in aqueous solutions was studied long back by Rigg et al. (1952).[1] They found that NH₃ was converted into NO₂⁻ in X-irradiated aerated solutions. In deaerated solutions however no nitrite was found. Pagsberg (1972) reported that the product in deaerated solutions was hydrazine.[2] The NH₂ radicals formed by the reaction of OH radicals with NH₃ are known to react with O₂ to form NH₂O₂ radicals which have absorption in the 290 nm region with $\epsilon = 1100 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. [3,4] The mechanism of formation of nitrite from this radical, however, is still not clear. We have estimated the yields of nitrite and H₂O₂ in aerated and oxygenated ammonia solutions at pH 10, and tried to arrive at a plausible mechanism for the formation of nitrite. The results are presented in this paper. G(H₂) values in irradiated ammonia solutions have also been measured. Implication of these results with respect to the use of NH₃ in the VVER coolant water is discussed.

In order to decrease the rate of corrosion caused mainly by radiolytic oxygen and hydrogen peroxide, hydrogen is introduced to the primary coolant of SMART which is an advanced integral reactor developed by Korea Atomic Energy Research Institute (KAERI). The water chemistry condition for SMART provides to allow its concentration to maintain at a level sufficient for suppression of water radiolysis and oxygen formation. Ammonia added to the primary coolant is decomposed by the action of radiation to generate molecular hydrogen and nitrogen. The decomposition of

ammonia, the source of hydrogen in the primary coolant is not quantitative: during stable normal operation, a certain state characterized by a constant ratio between concentrations of ammonia and its radiolysis and its radiolysis products (hydrogen and nitrogen) is established in the coolant. This ratio is determined, on the other hand, by ammonia radiolysis. Therefore, the ratio is dependent on the reactor power, ammonia dosage, and coolant composition; in particular the concentration of dissolved nitrogen in the coolant. In this paper kinetics of hydrogen and hydrogen peroxide from the radiolysis of ammonia was investigated as a function of ammonia concentration in water.

2. Experimental

All solutions were freshly prepared before each experiment with water purified using a NANO pure Diamond UV ultrapure water system from Barnstead International to remove organic and inorganic impurities. Prepared in this manner, the water had a resistivity of 18.2 M Ω -cm. The experiments at pH 6 were performed without the addition of any buffer, whereas those at pH 10.6 used a phosphate buffer (10⁻³ mol/dm³). The pH of the solution was measured prior to and at the end of the irradiation period using a pH meter (Symphony).

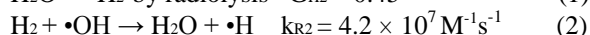
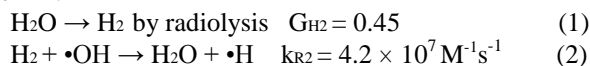
Ammonium hydroxide (NH₄OH) used for the experiment was of higher purity (sigma-Aldrich, $\geq 99\%$) and were used without further purification. The solutions were prepared freshly before each experiment with water purified using a NANO pure Diamond UV ultrapure water system from Barnstead International to remove organic and inorganic impurities. Prepared in this manner, the water had a resistivity of 18.2 Mohm-cm. The experiments were performed at both pH 6 and pH 10.6 without the addition of any buffer. The pH of the solution was measured before and after different time of irradiation using the pH meter (Symphony).

Irradiation was carried out in a ⁶⁰Co γ -cell (MDS Nordion), which provided the irradiation chamber with a uniform absorption dose rate of 2.5 Gy/s determined using Fricke dosimetry. The vials were placed in a specially designed sample holder so as to have a reproducible uniform dose during irradiation. Individual vials were taken out of the γ -cell at regular time intervals for H₂ and H₂O₂ analysis. Using a gas-tight syringe one half of the aqueous sample was transferred to another vial for H₂ analysis and the other half of the sample was used for aqueous analysis of H₂O₂.

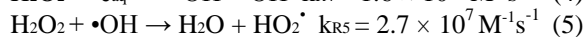
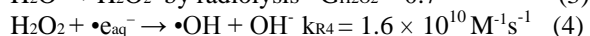
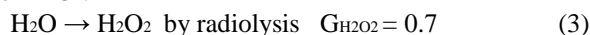
3. Results and Discussion

Detection of radical species during irradiation in the gamma cell is practically impossible due to their low concentrations and because of the space limit imposed upon by safety regulation. During irradiation, the radical species are continuously generated. The removal of the radiation source stops all further productions, and radicals decompose too rapidly for any post-irradiation analysis. However, molecular species do not decompose as fast and the post-irradiation detection of molecular species is possible. Thus, these species are the only measurable indicators of the redox condition of the system. Previously, a simple relationship between the concentrations of molecular species H_2 and H_2O_2 and radical species $\bullet OH$ and $\bullet e_{aq}^-$ has been derived for pure water systems based on a water radiolysis model [1] and experimental data. The kinetic analysis shows that the main production pathway for both H_2 and H_2O_2 is through primary radiolysis. The main decomposition pathway for H_2 is the reaction with $\bullet OH$ and for H_2O_2 , reactions with $\bullet e_{aq}^-$ and $\bullet OH$.

For H_2 :



For H_2O_2 :



The radiolysis of solutions containing initially $10^{-3} M$ NO_3^- generates higher H_2 concentrations relative to the pure water system under all conditions studied. The H_2 concentration in the presence of nitrate compared to pure water under aerated condition at pH 6 was shown in Fig. 1-a. This trend can be explained by considering the interactions of radiolytically produced nitrogen species with the $\bullet OH$ radical that controls the H_2 decomposition pathway. Nitrate itself is not an effective scavenger for $\bullet OH$, however, under the radiation conditions, it can be reduced to nitrite, NO_2^- , which is a good $\bullet OH$ scavenger (Reaction 6) and the level of $\bullet OH$ will be reduced relative to that of the pure water case (Figure 1-a). This decreases the H_2 decomposition by Reaction (2), so the observed H_2 concentrations are increased in the presence of dissolved nitrogen species, compared to pure water.

4. Conclusion

The effect of ammonia on gamma-water radiolysis was investigated in terms of kinetic analysis of H_2 and H_2O_2 . The kinetics of ammonia radiolysis was followed by monitoring the molecular water radiolysis products, H_2 and H_2O_2 , as well as NO_2^- and NO_3^- as a function of irradiation time. Steady-state water radiolysis entails a complex system of both reducing and oxidizing species with competing reactions occurring rapidly. In this work

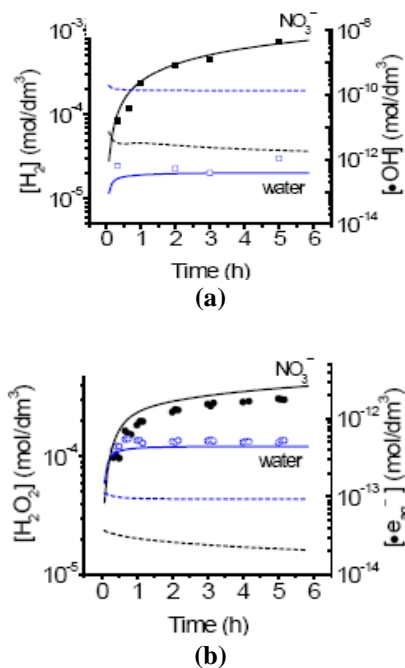


Figure 1. (a) $H_2(aq)$ and $\bullet OH$ and (b) H_2O_2 and $\bullet e_{aq}^-$ concentrations as a function of irradiation time under aerated conditions at pH 6.

both experiments and a kinetic model analysis were used to identify the effect of the pH and dissolved oxygen that dictate the concentrations of molecular radiolysis products. These concentrations depend on the concentrations of the free radicals that are generated by the radiolysis of ammonia and by the species that are used to control the solution redox and pH conditions (O_2 and OH^-). The observed rates for the radiolytic production of H_2 and H_2O_2 were analyzed using small reaction sets (Reaction 1 and Reaction 2 for H_2 , and Reaction 3 to Reaction 5 for H_2O_2). Differential equations were constructed from these simple reaction sets and were solved to yield the integrated rate equations for H_2 and H_2O_2 under the assumption that the radicals involved are at a steady-state concentration. This kinetic relationship verifies that the molecular species concentrations of H_2 and H_2O_2 are controlled by the behavior of $\bullet OH$ and $\bullet e_{aq}^-$. The combination of kinetic analysis for hydrogen and hydrogen peroxide by ammonia suggests that the concentrations of the key redox radical species can be determined from the measurements of H_2 and H_2O_2 .

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