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Gamma-Radiolysis of Aqueous Boric Acid Solution

Mitsuru KOIKE*, Enzo TACHIKAWA*
and Takao MATSUI**

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The γ-radiolysis of aqueous boric acid solutions of relatively high concentration has been studied. Boric acid significantly promotes hydrogen formation up to 10^{-7} mol/m*l* but does not increase oxygen and hydrogen peroxide to any appreciable extent. Since boric acid reacts at a relatively slow rate with species formed by the primary process of water radiolysis, when an effective scavenger for e_{aq}^- — the precursor of H_2 — such as NO_3^- is present, boric acid has no effects upon the total yield of H_2 in the range of concentrations studied. However, the yields of other products of the radiolysis — H_2O_2 and NO_2^- — are significantly reduced at high concentrations of boric acid when NO_3^- is present.

These results are explained by established reaction schemes for the radiolysis of aqueous solution. Based upon the behavior of NO_2^- from nitrate solutions, it is suggested that NO_2^- reacts with H_3BO_3 or H_2BO_3 radicals, the plausible reaction product from the reaction,

$$H_3BO_3 + OH \rightarrow H_2O + H_2BO_3.$$

I. INTRODUCTION

The use of a soluble neutron poison in the coolant of a large nuclear power reactor has the advantage of providing lower hot channel factors, thereby increasing the average power densities and fuel lifetimes. Among the possible materials available for this purpose, a dilute boric acid solution appears to be the most suitable.

While the amount of material actually used for the reactor coolant is not large, it nevertheless represents a significant modification of reactor coolant chemistry. It is essential for the successful design and operation of power reactors using soluble neutron poison that a clear insight be available concerning the basic chemical consequences of the addition of dilute boric acid upon irradiation with ionizing radiation.

Extensive work on boric acid and borate solutions undertaken in the French reactor Zoe have been reported by Bonet-Maury & Deysine(1) and Pucheault, Lefort & Haissinsky(2). These studies were carried out at relatively high concentrations of boric acid, the main emphasis being on hydrogen peroxide formation and decomposition. Hart, McDonell & Gordon(3) have irradiated boric acid solutions of zero to 0.2 M in the Argonne Heavy Water Reactor CP-3. A number of experiments have also been carried out using a loop installed in a power reactor(3)(4). Wright & Druga have bombarded a boric acid solution of 3.9B/*l* with electron beam, and have observed H_2 as sole product(5). This is in contradiction with the report of Hart *et al.*(3), who have observed H_2O_2 and H_2 in almost equal amounts. This discrepancy regarding resulting products can be attributed to difference in the radiation.

In the present work, the effect of the concentration of boric acid on the γ-radiolysis of aqueous boric acid solution was studied to gain knowledge on the chemical reactions produced by the boric acid with the reactive species formed by radiolysis.

II. EXPERIMENTS

The boric acid and sodium nitrate used in this work were obtained from Kanto Kagaku Co. Water was purified by triple distillation (ordinary distillation followed by distillations from acidic permanganate and dilute alkaline permanganate). The final distillate was

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* Japan Atomic Energy Research Institute, *Tokai-mura, Ibaraki-ken.*

** On leave of absence from the Faculty of Engineering, Chiba University, *Yayoi-cho, Chiba-shi.*

transferred into a measuring flask containing weighed boric acid either with or without additive.

The glassware used for the preparation of the solutions and for the irradiation was cleaned by steam for a couple of hours, and then pre-irradiated with γ-rays to 10^6R.

The sampling and analyzing techniques were essentially the same as reported by Rosenberg⁽⁶⁾. About 300 m*l* of boric acid solution was stored in a 500 m*l* flask provided with a side arm, to which 9 ampoules with a long tip were connected. The flask was equipped with a glass-coated magnetic stirrer to ensure complete degassing of the solution. After degassing, the whole apparatus was disconnected from the main vacuum line. Then each ampoule was sealed-off after it had been filled with the required amount of solution. Gas chromatographic analysis using Ar as carrier gas indicated that the content of air in each ampoule was less than 10^{-9} M. The oxygenated samples were prepared by introducing oxygen gas into the whole line after the complete degassing prior to seal-off.

The samples were irradiated at 30°C with γ-rays from a ^{60}Co source of 16 kCi at the Japan Atomic Energy Research Institute. The dose rate ranged from 1.25×10^5 to 1.05×10^5 R/hr. A Fricke Dosimeter, with $G(\mathrm{Fe}^{3+})=15.6$, was used for measuring the dose.

1. Analysis

The tip of the ampoule, set on the apparatus in the manner shown in **Fig. 1**, was broken in vacuum to transfer the whole solution into the reservoir. The gaseous products were extracted with a Toepler pump and directly injected into the gas chromatographic column for analysis (Gas chromatograph: Ohkura Rikaku, Model-6000). A molecular sieve 5A column 3 m long was used with a thermal conductivity detector at 25°C. Argon was used as carrier gas, flowing at 30 m*l*/min. Hydrogen peroxide was determined spectrophotometrically using the method developed by Ghormley⁽⁷⁾. The molar extinction coefficient of I_3^- was 24,500 $\mathrm{M}^{-1}\mathrm{cm}^{-1}$. Nitrite was also determined spectrophotometrically after reaction with sulfanilic acid and α-naphthylamine hydrochloride⁽⁸⁾.

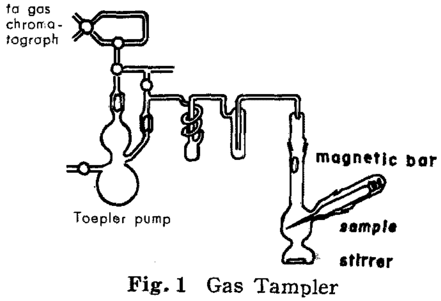

Fig. 1 Gas Tampler

III. RESULTS

While the conceivable products from the γ-radiolysis of aqueous boric acid solution are hydrogen, oxygen and hydrogen peroxide, the latter two products were not observed when no additive was present in the solution. This is in agreement with the observations reported by Wright & Druga⁽⁵⁾ upon electron bombardment of boric acid solutions, as well as with the results of γ-irradiation at the MTR Gamma Facility⁽⁵⁾.

In the subsequent experiments, the main emphasis was placed on the variation of hydrogen yield under various conditions. **Figure 2** shows the plots of the hydrogen yields in varying concentrations of boric acid as a function of total dose, up to 5×10^6R. The result for pure water is also shown in the same figure for reference. It is seen that hydrogen is not formed from pure water in irradiations up to 3×10^6R. However, with the boric acid solution, the yield of hydrogen rises abruptly upon dose initiation, and then already at about 1×10^5R it reaches a plateau value which depends on the concentration of boric acid. The plateau values of hydrogen yield are plotted in **Fig. 3** against the concentration of

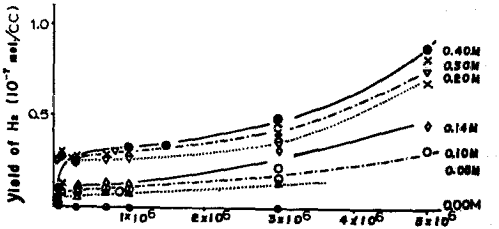

Fig. 2 Yield of H_2 from γ-irradiation of boric acid solution

boric acid. In the figure, the plateau value increases with the concentration but tends to be almost steady at above 0.3 M.

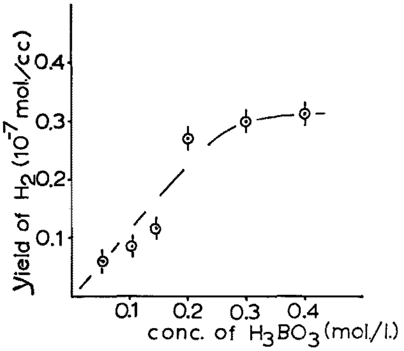

Fig. 3 Plateau value of H_2 yield (total dose $5\times10^5\sim1\times10^6$R)

Continued irradiation of the solution is seen in Fig. 2 to have caused a gradual further rise in the hydrogen yield above the plateau value at all boric acid concentrations. In connection with this observation, measurements of hydrogen yield from pure water at higher doses have also been made. The results, shown in **Fig. 4**, prove conclusively that the formation of hydrogen in the γ-radiolysis of water has been promoted by the presence of boric acid.

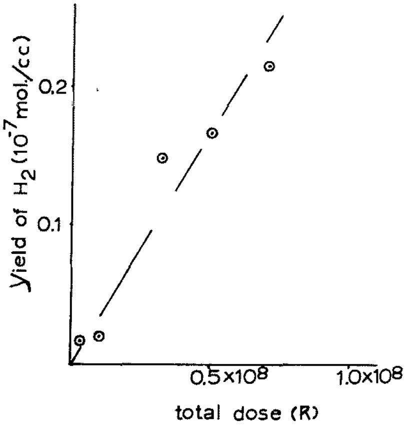

Fig. 4 Yield of H_2 from γ-irradiation of pure water

A plausible mechanism of this contribution of boric acid to the γ-radiolysis of water may be the dissociation of boric acid, producing hydrogen ions(9). The effect of hydrogen ion concentration on hydrogen formation from water has been extensively studied in the past by many workers(10)(11), but their reports are mostly concerned with the initial *G*-value. Moreover the results are not all quite in agreement with each other, and the values of $G(H_2)_{initial}$ range from 0.45 to 0.40. This $G(H_2)_{initial}$ measured in a number of different systems appear to indicate that the yields of hydrogen are slightly lower in acid than in neutral solution.

To examine the effect of hydrogen ions, the yield of hydrogen from sulfuric acid solution was also examined. The results from 10^{-4}, 10^{-3} and 10^{-1} M sulfuric acid solutions are plotted in **Fig. 5** against radiation dose. The result for 0.3 M boric acid solution, with a pH of 4.50, is also presented in the same figure for reference. These data on the two systems clearly prove that the effect of the hydrogen ion on the yield of hydrogen above 1×10^5R is not important.

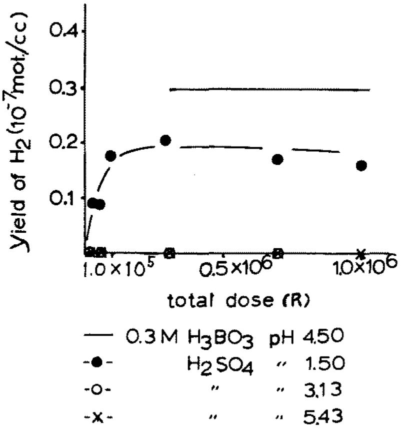

Fig. 5 Dependency of H_2 yield on pH

It is suggested that the effect of boric acid on the radiolysis of water may be explained in terms of the reaction of boric acid with the reactive species formed by irradiation. In order to elucidate the nature of such reactions, nitrate ion, which is known as an effective scavenger of solvated electrons, was added to the present system. A concentration of 10^{-2} M was chosen for the nitrate ion in the solution, which is high enough to scavenge quite effectively the solvated electrons in most of the solutions. In **Figs. 6, 7** and 8 are presented the yields of H_2, H_2O_2 and NO_2^- from 10^{-2} M sodium nitrate solutions containing boric acid in various concentrations, plotted against radiation dose. Up to 1×10^6R a linear relationship with irradiation dose is seen for the yields of H_2 and H_2O_2. From the slope of this line, the initial *G*-value can be calculated, the results being as summarized in **Table 1.**

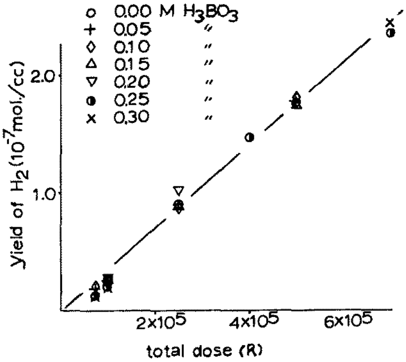

Fig. 6 Hydrogen formation from sodium nitrate solution containg boric acid

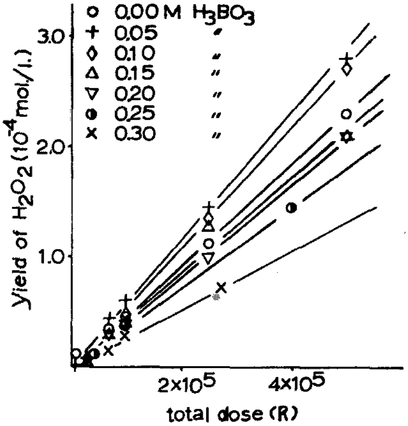

Fig. 7 Hydrogen peroxide formation from sodium nitrate solution containing boric acid

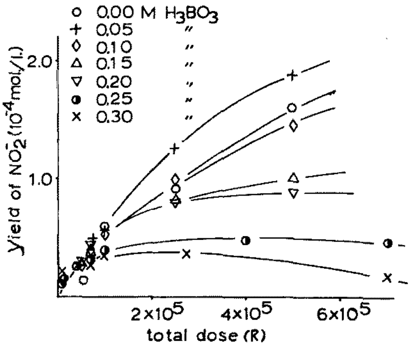

Fig. 8 Nitrite ion formation from sodium nitrate solution containing boric acid

Table 1 Yields of products from γ-irradiation of air-free 10^{-2} M $NaNO_3$ solution containing boric acid

Conc. of H_3BO_3(M)	Press. of O_2 applied (cmHg)	$G(H_2)_{initial}$	$G(H_2O_2)_{initial}$
0†	0	0.45	0.70
0	0	0.37±0.02	0.46±0.02
0.05	0	0.37±0.02	0.59±0.02
0.10	0	0.37±0.02	0.51±0.02
0.15	0	0.37±0.02	0.43±0.02
0.20	0	0.37±0.02	0.40±0.02
0.25	0	0.37±0.02	0.33±0.02
0.30	0	0.37±0.02	0.22±0.02
0.30	20	0.38±0.02	—
0.30	76	0.37±0.02	—
0.05††	76	—	0.60±0.02
0.30††	76	0.11±0.02	0.21±0.02

† for pure water(11)
†† in absence of $NaNO_3$

It is seen from this table that the addition of boric acid to the sodium nitrate solution has no effect on $G(H_2)_{initial}$, but on the other hand markedly affects $G(H_2O_2)_{initial}$.

In contrast to the foregoing data on H_2 and H_2O_2, the yield of NO_2^- (**Fig. 8**) is characterized by a complicated dependence on radiation dose and on concentration of boric acid.

IV. DISCUSSIONS

The primary decomposition of pure water by ionizing radiation leads to the formation of the following reactive species and molecular products in spurs: e_{aq}^-, OH, H, H_2O_2, H_2 and H_3O^+(12). The molecular products formed will, however, rapidly react with the reactive species to recombine into water.

$$H_2+OH \rightarrow H_2O+H \tag{1}$$

$$H_2O_2+H \rightarrow H_2O+OH \tag{2}$$

$$H_2O_2+e_{aq}^- \rightarrow OH^-+OH \tag{3}$$

Thus, when solely pure water is present, no net effect of radiolysis will be observed. When however, a solute that reacts with these reactive species is present in the system, it may intervene in the foregoing reactions and increase the yield of the molecular products.

Among the conceivable reactions between boric acid and the reactive species involved in the radiolysis, the following are proposed for explaining our findings.

$$H_3BO_3 + e^-_{aq} \rightarrow H + H_2BO_3^-, \qquad (4)$$

$$H_3BO_3 + H \rightarrow H_2 + H_2BO_3, \qquad (5)$$

$$H_3BO_3 + OH \rightarrow H_2O + H_2BO_3. \qquad (6)$$

The rate constants for reactions (4) and (6) have been established photochemically by Ohno(13)(14) to be 3×10^6 and $1.9\times10^8\,M^{-1}\cdot sec^{-1}$ respectively. While no data have been published concerning reaction (5), the rate constant may be quite small.

The foregoing behavior of boric acid can be explained in terms of the competition between boric acid and hydrogen for the OH radical (reaction (6)). Since the rate constants for reactions (1) and (6) do not differ largely from each other(15), reaction (6) would preponderate over the reaction (1) at the early stages of radiolysis. This explains the sharp initial increase of hydrogen yield seen in Fig. 2. As hydrogen builds up to the extent that reaction (1) starts to compete with reaction (6), the net rate of hydrogen formation will rapidly slow down.

Now, if only reaction (1) comes into play for the destruction of the hydrogen molecules thus formed, the yield should continue increasing with dose so long as boric acid is present in sufficient quantity to scavenge all the OH radicals. In actuality, experimental data indicate the existence of the plateau range even with boric acid solution of concentration as high as 0.40 M. This is a value that can be considered ample for complete scavenging of OH radicals. The above circumstances would imply the concurrent involvement of reactions other than that of the OH radical in the mechanism of H_2 elimination from the present system. Plausible additional reactions would be those of H_2 with H_2BO_3 by reactions (5) and (6).

A gradual increase in hydrogen yield at higher radiation doses can be seen with boric acid solutions. A similar trend is also observed with pure water (Fig. 4), although the radiation dose required to prove this is much larger than for boric acid solution. This would be due to the hydrogen diffused out into the gas phase, rather than that formed outside the spurs.

As each ampoule was filled with solution only to 2/3 of its total volume, a part of the hydrogen formed during irradiation in the solution will have diffused out into the gas phase, and such hydrogen will have been involved in no further reaction with the reactive species. Since the rate of diffusion of the hydrogen molecules into the gas phase is proportional to its concentration in the liquid phase, the hydrogen yield should increase faster the higher the concentration of boric acid, which is precisely what was observed from experiment. A preliminary experiment showed that the yield of hydrogen at 5×10^6 R is a function of the volume of gas in the irradiating ampoule, so that higher yields resulted from ampoules containing larger volumes of gaseous phase. This is consistent with the above discussion.

As a collorary to the above discussion, it might be considered that the slope of the line in Fig. 4 would indicate the diffusing rate of hydrogen into the gas phase under irradiation. Furthermore, the rate should depend upon the relative volume of the gas phase present. The range of experimental data available here, however, does not allow us to pursue this discussion much further.

Increasing the concentration of additive raised to an appreciable rate the reactions of the additive with the reactive species resulting from the radiolysis of water within the spurs, and correspondingly reduced the recombination of the reactive species producing the molecular products. This can be associated with the observed decrease in the initial *G*-value of molecular products with increasing additive concentration(16). The relatively slow reactions of boric acid with the reactive species may suggest a slight decrease of the initial *G*-value of molecular hydrogen with increasing concentration of boric acid. In the present work, quantitative estimation of the initial *G*-value of hydrogen was not obtained, but qualitatively, the above argument has been confirmed.

H_3BO_3-$NaNO_3$ system

In addition to the reactions (4), (5) and (6), a number of other reactions are also conceivable in the system under consideration:

$$NO_3^- + e_{aq}^- \rightarrow NO_2 + 2OH^- \quad k = 8.15\times10^9\ \mathrm{M^{-1}\cdot sec^{-1}} \qquad (7)^{(17)(18)}$$

$$NO_3^- + H \rightarrow NO_2 + OH \quad k = 5.4\times10^8,\ 1.0\times10^9\ '' \qquad (8)^{(19)(20)}$$

$$NO_3^- + OH \rightarrow \quad \cdots\cdots\cdots\cdots \qquad (9)$$

$$NO_2^- + e_{aq}^- \rightarrow \quad k = 4.58\times10^9,\ 3.45\times10^9\ '' \qquad (10)^{(17)(21)}$$

$$NO_2^- + H \rightarrow NO + OH^- \quad k = 1.4\times10^9,\ 4\times10^8\ '' \qquad (11)^{(20)(22)}$$

$$NO_2^- + OH \rightarrow \quad k = 2.4\times10^9\ '' \qquad (12)^{(22)(23)}$$

The linear increase observed in the yield of hydrogen and hydrogen peroxide in the sodium nitrate solution in keeping with mounting dose would be due to the protection provided by the nitrite ion on these products from back reactions. The slopes of the lines in Figs. 6 and 7 indicate $G(H_2)$ and $G(H_2O_2)$ to be 0.37 and 0.46, respectively, both these values being smaller than the initial *G*-values for pure water.

The decrease in $G(H_2)$ from 0.45 for pure water to 0.37 in this system (Table 1) can be accounted for by the scavenging of nitrate ion of e_{aq}^-, one of the precursors for H_2 (reaction (7)). When boric acid is added to this solution, reaction (4) becomes possible in addition to reaction (7). However, under the concentrations in question with respect of these additives, reaction (7) will proceed roughly 10^3 times faster than reaction (4). Thus, boric acid is not important for the formation of hydrogen in this system, and therefore there is no concentration dependence of boric acid on the yield of hydrogen, which is what is revealed in Fig. 6. Furthermore, it can be proved that the amount of hydrogen produced by the reactions (4) and (5) is not significant.

On the other hand, the effect on $G(H_2O_2)$ of the addition of boric acid to sodium nitrate solution is first a sharp increase, followed by linear decrease upon further addition (Fig. 7). The appearance of this maximum in $G(H_2O_2)$ can be interpreted as follows: boric acid can be considered to affect the $G(H_2O_2)$ in two ways, one to scavenge by reactions (4)~(6) the bulk of the reactive species in the solution to reduce the back reaction of H_2O_2, and the other is the reaction (6) tending to reduce the recombination of two OH radicals to form H_2O_2 in the spurs. At low concentrations of boric acid, the former is predominant and $G(H_2O_2)$ increases, but as the concentration is increased the latter will also become significant.

The yield curve of NO_2^- shows a somewhat different behavior from that for H_2O_2. The data do not reveal in this case a straight forward linear relationship between yield and dose. The characteristic effects brought by the presence of boric acid on NO_2^- formation are well represented in the solution containing 0.30 M boric acid: The yield curve reaches a maximum of 3.6×10^{-5} M at 2.75×10^5 R, from where it falls to 4.5×10^{-6} M at 3.0×10^6 R.

The formation of nitrite ion can be explained by the following reaction sequence$^{(11)}$:

$$NO_3^- + e_{aq}^- \rightarrow NO_2 + 2OH^-, \qquad (7)$$

$$2NO_2 + H_2O \rightarrow NO_2^- + NO_3^- + 2H^+. \qquad (13)$$

The first step is fast but the second is believed to be slow$^{(11)}$. In the early stage of the radiolysis of sodium nitrate solution, NO_2^- is accumulated with increasing dose, which corresponds to the linear part of the curve shown in Fig. 8. When NO_2^- is accumulated in enough quantity to react with the OH radical, the overall rate of production of NO_2^- then is slowed down.

In the presence of boric acid, reaction (6) will compete with reaction (12) and as the concentration of boric acid increases, reaction (12) will become less prominent. Accordingly, an explanation for the yields of NO_2^- obtained in H_3BO_3-$NaNO_3$, is to assume that NO_2 formed by the reduction of NO_3^- does not disproportionate *via.* the slow reaction (13) but partly disappears through the reaction with the H_3BO_3 or H_2BO_3 radical, the plausible reaction product from reaction (6).

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