5.6 Radiolysis of Concentrated Nitric Acid Solutions

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Abstract A study on electron pulse- and ^{60}Co γ-radiolysis of concentrated nitric acid and nitrate solutions has been carried out to elucidate the radiation induced reactions taking place in the solutions. Dissociation into NO_2^- and $O(^3P)$ was proposed as a direct action of the radiation on nitrate and gave the G-values were dependent on the chemical forms of nitrate: $g_{s2}(-NO_3^-)=1.6$ and $g_{s2}(-HNO_3)=2.2$ (molecules/100eV). Based on the experimental yields of HNO_2 and reduced Ce^{IV}, the primary yields of radiolysis products of water, g_w, were evaluated to clarify the effects of nitrate on spur reactions of water in various nitrate solutions.

INTRODUCTION

While the understanding of the radiolysis of diluted aqueous solutions was well established, that of concentrated solutions is far from complete. Because the solute as well as water can absorb the energy of radiation in the solutions and intermediates are directly formed from the solute (direct action), which react with the radiolysis products of water(indirect action) leading the reaction scheme in the solutions to be complicated. We have been studying the radiolysis of concentrated acid solutions to understand and predict the radiation induced reactions taking place in the solutions.

In the present experiment, the radiolysis of concentrated nitric acid and nitrate solutions has been studied and reported[1-3], which is practically related to the radiation effects in the nuclear spent fuel reprocessing. NO_3 radical was observed using the pulse radiolysis method with electron pulses and yields of HNO_2 formed and Ce^{IV} reduced in γ-radiolysis were obtained. On the basis of the experimental results, the radiolytic processes of nitrate were proposed together with the yields and the radiation induced reactions were discussed quantitatively.

EXPERIMENTAL

Electron pulses of 100 ns and 28 MeV from a linear accelerator at Nuclear Engineering Research Laboratory and γ-ray from 3kCi ^{60}Co at Rearch Center for Nuclear Science and Technology, University of Tokyo, were used.

Details of the pulse radiolysis system have been described elsewhere.[1] The absorbance of NO_3 radical was followed at 640 nm, where the spectrum of NO_3 have a peak($\epsilon=1300\pm100$ M$^-$ ^{1}cm^{-1}). For the dosimetry, a 10 mM KSCN aqueous solution saturated with N_2O was used with G=6.1 (molecules/100eV) and $\epsilon(472nm)=7580$ M^{-1}cm^{-1} for the radical anion $(SCN)_2^-$.

Ar-purged nitric acid solutions were irradiated by γ-ray with the dose rate of 1.4 Gy·s^{-1} to determine the yields of HNO_2 formed as the final product, and aerated nitrate solutions containing Ce^{IV} ion irradiated with 0.02-0.14 Gy·s^{-1} to determine yields of reduced Ce^{IV}. HNO_2 was determined using Shinn's method with some modification with the

$\varepsilon(543\text{nm})=53400$ $M^{-1}cm^{-1}$ as estimated in this study.[2] The absorption coefficients of Ce^{IV} in various nitrate solutions were also estimated.[3] For the dosimetry, the Fricke dosimeter was used with $G=15.5$ and $\varepsilon(304\text{nm})=2164\,M^{-1}cm^{-1}$ for Fe^{3+}.

All experiments were carried out at room temperature(around 20 °C) unless otherwise stated. The energy deposition was assumed to be proportional to the electron density of the solutions and was corrected accordingly.

<div align="center">RESULTS AND DISCUSSION</div>

Expression of observed G-value

When a species P is formed in the radiolysis of concentrated nitrate solutions, the yield of P, $G(P)$, can be expressed as a function of electron fraction of nitrate(f_s) as a solute :

$$G(P) = g_w \cdot f_w + g_s \cdot f_s \qquad ; f_w + f_s = 1 \qquad . \qquad (I)$$

, where g_w and g_s are the yields of radiolysis products originated from nitrate(ion form NO_3^- and acid form HNO_3) and water, respectively, which form P after escaping from spurs. f_s is given by $f_s=[SN_S/M_S]/[SN_S/M_S+ (1-S)N_W/M_W]$, where S is the wt.% of nitrate, $N_S(=32)$ and $N_W(=10)$ are the molecular numbers of nitrate and water, and M_S and M_W the molecular weights of nitrate and water, respectively. The energy of radiation was assumed to be absorbed not by only valence electrons but by all valence and inner-sphere electrons.

Radiolytic processes of nitrate

NO_3 radical has been observed as an intermediates from nitrate, which has characteristic peaks at 600, 640, and 675 nm in its spectrum.[1] It was found in the pulse-radiolysis experiments that NO_3 was formed through a dissociation of nitrate(fast process)(1) and the reaction of undissociated HNO_3 with OH radical(slow process)(2) :

$$NO_3^- \xrightarrow{\sim\!\sim\!\sim\!\sim} NO_3 + e_{aq}^- \qquad (1)$$

$$OH + HNO_3 \rightarrow H_2O + NO_3 \qquad ; k = 1.4 \times 10^8\,M^{-1}s^{-1} \qquad . \qquad (2)$$

Fig.1 shows the experimental yields of NO_3, $G(NO_3)$, against f_s. The fast process was independent of chemical forms of nitrate and gave a relation of $g_{S1}(NO_3)=g_{S1}(e_{aq}^-)=g_{S1}(-NO_3^-)=g_{S1}(-HNO_3)=4.8$ (molecules/100eV).
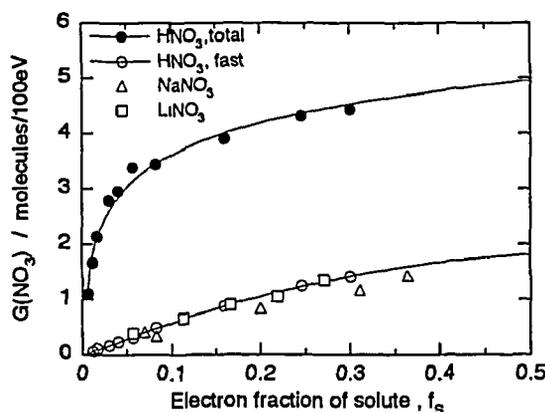

Figure 1 Dependence of $G(NO_3)$ on nitric Acid and nitrate concentrations.

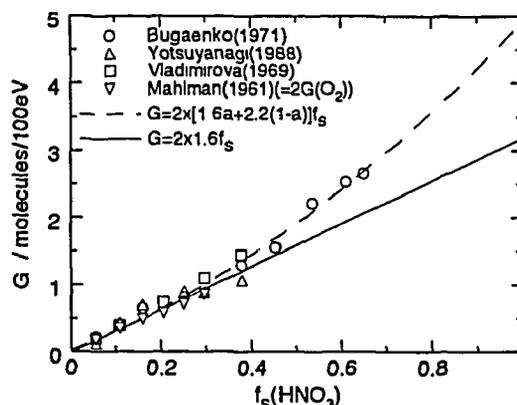

Figure 2 G-values of HNO_2 and O_2 in nitric acd solutions. a : dissociation degree of nitric acid

HNO_2 and O_2 are formed as final products in γ-radiolysis of concentrated nitrate solutions. The experimental yields of HNO_2 and O_2 have been reported by us and the other groups as shown in Fig.2.[2] There are not any contributions of water radiolysis and the fast process of NO_3 (1), [2] suggesting the existence of other radiolysis process(es) leading to the formation of HNO_2 and O_2. Since at $f_S<0.4$ in Fig.2, the ratio of $G(HNO_2)/G(O_2)$ was 2 as reported by Mahlman[5], the following dissociation and reaction were proposed :

$$NO_3^- \rightsquigarrow NO_2^- + O\ (^3P) \tag{3}$$

$$O(^3P) + NO_3^- \rightarrow O_2 + NO_2^- \quad . \tag{4}$$

The formed $O(^3P)$ can react with NO_3^- but not with water. The dissociation of nitrate into NO_2 and $O^-(OH)$ as the other radiolysis process was not taken into account in the present work because of no formation of HNO_2 and O_2. Also Fig.2 shows that the experimental $G(HNO_2)(=2f_S \cdot g_{S2}(NO_2^-))$ did not increase linearly with f_S at $f_S>0.4$, suggesting that the dissociation was dependent on the forms of nitrate. g_{S2} could be expressed by the dissociation degree of nitric acid, α.

$$g_{S2}(NO_2^-) = g_{S2}(O) = \alpha \cdot g_{S2}(-NO_3^-) + (1-\alpha) \cdot g_{S2}(-HNO_3) \tag{II}$$

$g_{S2}(-NO_3^-)=1.6$ (molecules/100eV) was evaluated from $G(HNO_2)$ at $f_S<0.4$ and $g_{S2}(-HNO_3)=2.2$ at $f_S> 0.4$.

Radiolytic reduction of Ce^{IV}

Since NO_3^- is well known to be a strong scavenger of pre-hydrated(e_p^-) and hydrated (e_{aq}^-) electrons, the primary yields of water radiolysis may change with nitrate concentration.

$$e_p^-\ /\ e_{aq}^- + NO_3^- + H_2O \rightarrow NO_2 + 2OH^- \rightarrow 1/2\ HNO_2 \tag{5}$$
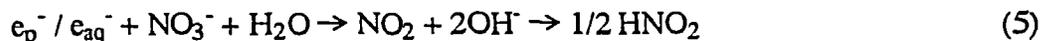
In order to understand the effects of nitrate on the primary yields of the radiolysis products of water, aerated 0.4 M sulfuric acid with nitric acid or sodium nitrate solutions containing cerium ion were irradiated and analysed for the yield of Ce^{IV}. Fig.3(a) shows the yields of reduced Ce^{IV}, $G(-Ce^{IV})$, in the absence(G_1) and presence(G_2) of Tl^+. [3]
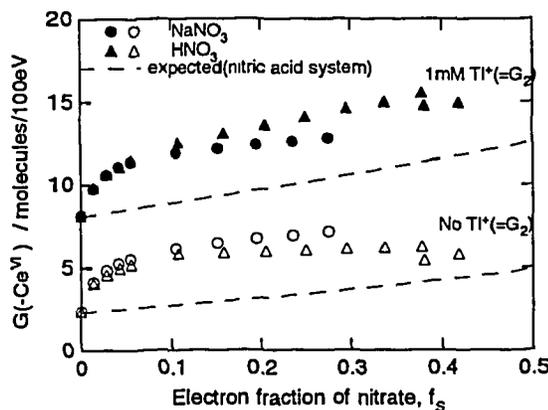

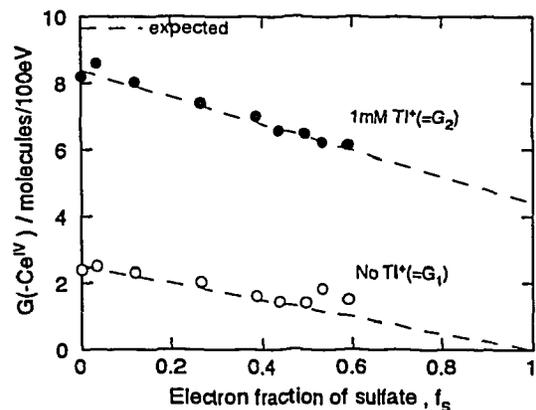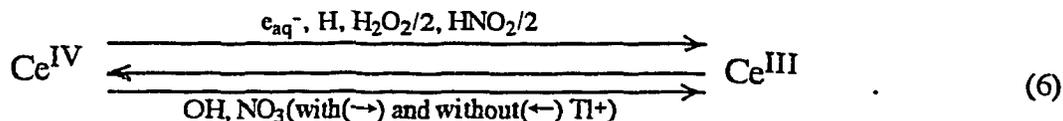Figure 3(a) The yield of Ce^{IV} reduced in 0.4M H_2SO_4

Figure 3(b) The yield of Ce^{IV} reduced in H_2SO_4 solutions

In the radiolysis, the redox of cerium ions with the radiolysis products of water and nitrate could occur as follows :

$$\text{Ce}^{IV} \xrightleftharpoons[\text{OH, NO}_3(\text{with}(\rightarrow) \text{ and without}(\leftarrow) \text{ Tl+})]{e_{aq}^-, \text{ H, H}_2\text{O}_2/2, \text{ HNO}_2/2} \text{Ce}^{III} \qquad . \qquad (6)$$

Consequently, the $G(-\text{Ce}^{IV})$, could be expressed using the yields of the radiolysis products :

$$G_1(-\text{Ce}^{IV}) = f_{W}\cdot[g_W(e_{aq}^-+H) - g_W(\text{OH}) + 2g_W(\text{H}_2\text{O}_2)] + f_{S}\cdot[g_{S1}(e_{aq}^-) - g_{S1}(\text{NO}_3)]$$
$$+4f_{S}\cdot[\alpha\cdot g_{S2}(-\text{NO}_3^-) + (1-\alpha)\cdot g_{S2}(-\text{HNO}_3)] \qquad (III)$$

$$G_2(-\text{Ce}^{IV}) = f_{W}\cdot[g_W(e_{aq}^-+H) + g_W(\text{OH}) + 2g_W(\text{H}_2\text{O}_2)] + f_{S}\cdot[g_{S1}(e_{aq}^-) + g_{S1}(\text{NO}_3)]$$
$$+4f_{S}\cdot[\alpha\cdot g_{S2}(-\text{NO}_3^-) + (1-\alpha)\cdot g_{S2}(-\text{HNO}_3)] \qquad . \qquad (IV)$$

When the primary yields of radiolysis products of water in 0.4M sulfuric acid were used as g_W in eqn.(III) and (IV), G_1 and G_2 could be expected, plots of which are shown as dotted lines(nitric acid) in Fig.3(a). However, the lines did not agree with the experimental $G(-\text{Ce}^{IV})$.

On the other hand, $G(-\text{Ce}^{IV})$ in sulfuric acid solutios agreed well with the expected lines as shown in Fig.3(b), where the dissociation into SO_4^- and e_{aq}^- only takes place as the radiolysis of sulfate.[4] These results suggests that NO_3^- and HNO_3 have influences on the spur reactions of water and that the respective g_W vary with the concentration of nitrate.

The primary yields of radiolysis products of water

The respective g_W of $-\text{H}_2\text{O}$, $e_{aq}^-+\text{H}$, OH, and H_2O_2 can be evaluated from the material balance(V) and the experimental yields of g_{S1}, g_{S2}, G_1 and G_2 in the following equations :[3]

$$g_W(-\text{H}_2\text{O}) = g_W(e_{aq}^-+H) + 2g_W(\text{H}_2) = g_W(\text{OH}) + 2g_W(\text{H}_2\text{O}_2) \qquad (V)$$

$$g_W(\text{OH}) = \{[G_2(-\text{Ce}^{IV}) - G_1(-\text{Ce}^{IV})]/2 - f_{S}\cdot g_{S1}(\text{NO}_3)\}/f_W \qquad (VI)$$

$$g_W(-\text{H}_2\text{O}) = \{G_2(-\text{Ce}^{IV}) + 2G(\text{H}_2) - 2 f_{S}\cdot g_{S1}(\text{NO}_3) - 4f_{S}\cdot[\alpha\cdot g_{S2}(-\text{NO}_3^-) +$$
$$(1-\alpha)\cdot g_{S2}(-\text{HNO}_3)]\}/(2f_W) \qquad (VII)$$

$$g_W(e_{aq}^-+H) = g_W(-\text{H}_2\text{O}) - 2g_W(\text{H}_2) \qquad (VIII)$$

$$g_W(\text{H}_2\text{O}_2) = [g_W(-\text{H}_2\text{O}) - g_W(\text{OH})]/2 \qquad (IX)$$

, where $g_W(\text{H}_2)$ is obtained from $G(\text{H}_2)$ ($=g_W(\text{H}_2)\cdot f_S$) reported by Mahlman.[5] Fig.4 shows the g_W in 0.4M sulfuric acid with nitric acid(a) and sodium nitrate(b).

In both the nitric acid and sodium nitrate systems, the $g_W(-\text{H}_2\text{O})$ and $g_W(e_{aq}^-+H)$ concurrently increase with the concentration of nitrate, while the $g_W(\text{H}_2)$ decreases. It indicates clearly that the electron scavenging of NO_3^- in spurs suppresses recombinations between e_{aq}^- and OH into water and H_2 formation from the reaction of a pair of e_{aq}^-. Furthermore, the $g_W(-\text{H}_2\text{O})$ at higher f_S is larger than the recommended initial yield of water decomposition(=5.7), suggesting the yield larger than 5.7 in concentrated nitrate solutions just after water

decomposition by radiation.

Consequently, the yields of OH escaping from spurs and H_2O_2 formed from a pair of OH would be expected to increase. However, the tendency of the $g_W(OH)$ and $g_W(H_2O_2)$ in the nitric acid system are different from those in the sodium nitrate system. Because not only NO_3^- but also HNO_3 exsists in the nitric acid system, the OH scavenging of HNO_3 suppresses the H_2O_2 formation. Therefore, the $g_W(OH)$ increases and the $g_W(H_2O_2)$ does not vary in the nitric acid system, while the $g_W(OH)$ decreases and the $g_W(H_2O_2)$ increases in the sodium nitrate system.

Also the yield of O_2, $G(O_2)$, in nitrate solutions in the absence(X) and the presence(XI) of Ce^{IV} can be evaluated:

$$G(O_2) = f_S \cdot g_{S2}(O) \qquad\qquad (X)$$

$$G(O_2) = f_W \cdot g_W(H_2O_2) + f_S \cdot g_{S2}(O) = [G_1(-Ce^{IV}) + 2f_W \cdot g_W(H_2)]/4 \qquad (XI)$$

$G(O_2)$ evaluated in 0.4M sulfuric acid with Ce^{IV}-sodium nitrate is found to increase with f_S and agree well with that reported by Mahlman.[5]
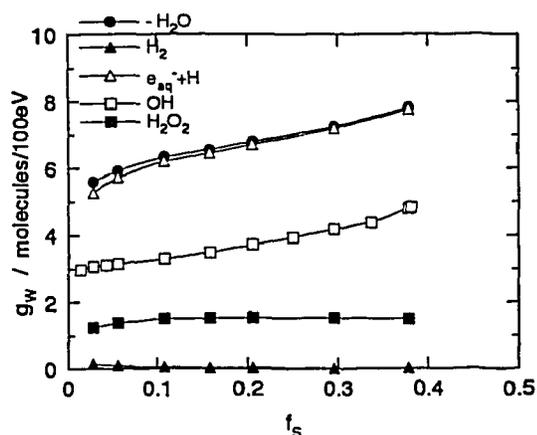

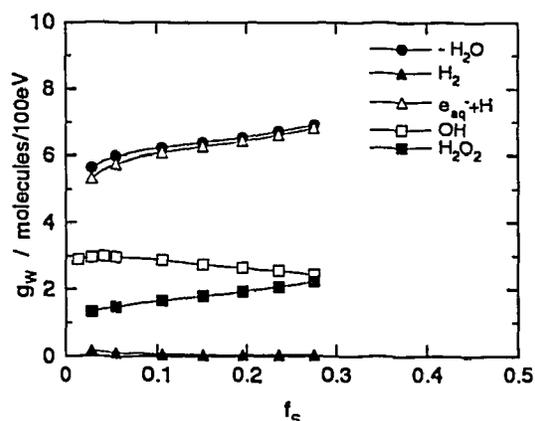Figure 4(a) The primary yields of water radiolysis in 0.4M sulfuric acid solution with nitric acid

Figure 4(b) The primary yields of water radiolysis in 0.4M sulfuric acid solution with sodium nitrate

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