J. CHEM. SOC. FARADAY TRANS., 1994, 90(4), 591–595

# Primary Yields of Water Radiolysis in Concentrated Nitric Acid Solutions

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The primary yields of water radiolysis have been evaluated as a function of nitric acid or nitrate concentration in the $^{60}$Co $\gamma$-radiolysis of nitric acid and 0.4 mol dm$^{-3}$ sulfuric acid with nitric acid or sodium nitrate solutions containing Ce$^{IV}$ and Ce$^{III}$, in the presence and absence of Tl$^+$. The radiolytic decomposition of water is significantly enhanced in these systems, from $g_w(-H_2O) = 0.60$ µmol J$^{-1}$ for 0.4 mol dm$^{-3}$ sulfuric acid–sodium nitrate solutions to $g_w(-H_2O) = 0.76$ µmol J$^{-1}$ for nitric acid solutions at high solute concentrations.

In order to understand the radiolysis of concentrated nitric acid solutions, we have studied the direct action of radiation of nitric acid, which has been shown to give rise to $NO_3 + e_{aq}^-$ and $O + NO_2^-$.[1,2] Since nitrate anion is a strong scavenger of pre-hydrated ($e_p^-$) and hydrated ($e_{aq}^-$) electrons,[3–5] the radiolysis of water is significantly influenced in nitric acid solutions, which is evident from the fact that the radiolytic reduction of the Ce$^{IV}$ to Ce$^{III}$ is remarkably enhanced in nitric acid and acidic nitrate solutions.[6–13] However, there seems to have been no estimation of the primary yields of water radiolysis in concentrated nitric acid and acidic nitrate solutions, which are indispensable for a fuller understanding of the radiolytic processes. The radiolytic reduction of Ce$^{IV}$ to Ce$^{III}$ in nitric acid, 0.4 mol dm$^{-3}$ sulfuric acid–nitric acid and 0.4 mol dm$^{-3}$ sulfuric acid–sodium nitrate solutions in the presence and absence of Tl$^+$ has been studied in the present work with $^{60}$Co $\gamma$-radiation. The primary yields of water radiolysis have been evaluated as a function of nitric acid or nitrate concentration for these systems.

## Experimental

Nitric acid solutions, sodium nitrate and other chemicals were of the highest available purity and were used as supplied. The water was purified by distillation followed by filtration through a millipore system. Aerated solutions were irradiated at room temperature with a 3 kCi $^{60}$Co $\gamma$-source, which provided dose rates in the range 0.02–0.14 Gy s$^{-1}$ as determined by the Fricke dosimeter with $G(Fe^{3+}) = 1.62$ µmol J$^{-1}$. The concentrations of Ce$^{IV}$ were measured spectrophotometrically using molar absorption coefficients determined in the present study. The energy deposition was assumed to be proportional to the electron density and was corrected accordingly.

## Results and Discussion

### Molar Absorption Coefficients (ε) of Ce$^{IV}$

Stock solutions of 4 mmol dm$^{-3}$ $Ce(SO_4)_2$ in 0.4 mol dm$^{-3}$ sulfuric acid were prepared and the concentration of Ce$^{IV}$ as determined on the basis of ε(Ce$^{IV}$, 320 nm) = 561 m$^2$ mol$^{-1}$ at 298 K in 0.4 mol dm$^{-3}$ sulfuric acid solutions.[14] Solutions of 0.4 mol dm$^{-3}$ sulfuric acid with nitric acid or sodium nitrate containing 0.2–0.4 mmol dm$^{-3}$ $Ce(SO_4)_2$ were prepared by diluting the stock solutions and the concentrations of Ce$^{IV}$ were calculated. The absorbances of the solutions were measured and the molar absorption coefficients of Ce$^{IV}$ were evaluated at selected wavelengths in the range 350–420 nm. The decadic ε(Ce$^{IV}$, 370 nm) values obtained are shown in Table 1 for 0.4 mol dm$^{-3}$ sulfuric acid–nitric acid solutions and 0.4 mol dm$^{-3}$ sulfuric acid–sodium nitrate solutions. For nitric acid solutions, a weighed amount of anhydrous $(NH_4)_2Ce(NO_3)_6$ was dissolved into the solutions and the concentrations of Ce$^{IV}$ (0.2–0.6 mmol dm$^{-3}$) were calculated. The decadic ε(Ce$^{IV}$, 370 nm) values obtained are also shown in Table 1. The determination of Ce$^{IV}$ in irradiated solutions was carried out at several wavelengths in the range 350–390 nm where only Ce$^{IV}$ absorbs. The measurement and the molar absorption coefficients of Ce$^{IV}$ are not affected by the presence of Ce$^{III}$ and Tl$^+$, at least in the wavelength range 350–390 nm.

### Yields of Radiolytic Reduction of Ce$^{IV}$ to Ce$^{III}$

Aerated nitric acid and 0.4 mol dm$^{-3}$ sulfuric acid with nitric acid or sodium nitrate solutions containing Ce$^{IV}$ and Ce$^{III}$ with or without Tl$^+$ were irradiated and analysed for Ce$^{IV}$. The concentrations of Ce$^{IV}$ were 0.4–0.6 mmol dm$^{-3}$ before irradiation and the ratios of [Ce$^{III}$]/[Ce$^{IV}$] were kept between

**Table 1** Molar absorption coefficients (370 nm) of Ce$^{IV}$ (m$^2$ mol$^{-1}$)

| $[HNO_3]$/mol dm$^{-3}$ | ε/m$^2$ mol$^{-1}$ | $[NaNO_3]$/mol dm$^{-3}$ | ε/m$^2$ mol$^{-1}$ | $[HNO_3]$/mol dm$^{-3}$ | ε/m$^2$ mol$^{-1}$ |
|---|---|---|---|---|---|
| 0 | 253 | | | | |
| 0.25 | 250 | 0.25 | 258 | 0.14 | 40.5 |
| 0.50 | 249 | 0.50 | 262 | 0.60 | 63.5 |
| 0.75 | 250 | 0.75 | 266 | 0.81 | 75.3 |
| 1.0 | 253 | 1.0 | 269 | 1.1 | 89.0 |
| 2.0 | 266 | 2.0 | 278 | 2.2 | 135 |
| 3.0 | 283 | 3.0 | 283 | 3.1 | 178 |
| 4.0 | 304 | 4.0 | 286 | 4.2 | 219 |
| 5.0 | 329 | 5.0 | 288 | 5.1 | 303 |
| 6.0 | 357 | 6.0 | 289 | 6.1 | 390 |
| 7.0 | 387 | — | — | 7.1 | 445 |
| 8.0 | 417 | — | — | 8.1 | 470 |

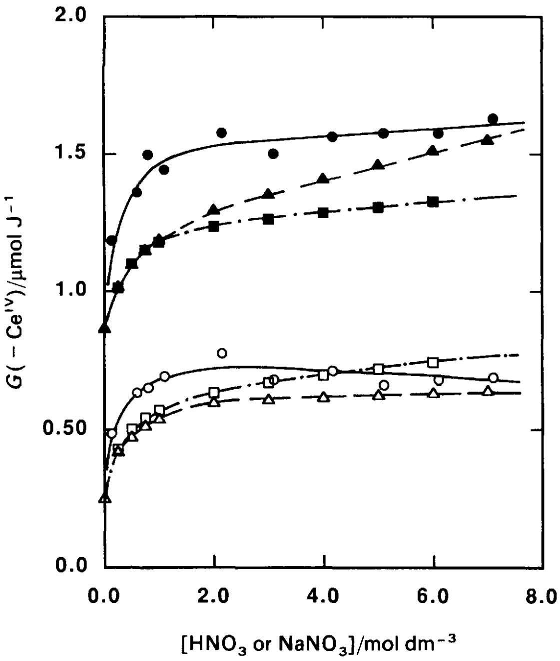

**Fig. 1** Yields of radiolytic reduction of $Ce^{IV}$ to $Ce^{III}$ in the presence and absence of $Tl^+$ in nitric acid and 0.4 mol $dm^{-3}$ sulfuric acid with nitric acid or sodium nitrate solutions. Nitric acid: (○) without $Tl^+$; (●) 5.0 mmol $dm^{-3}$ $Tl^+$. 0.4 mol $dm^{-3}$ sulfuric acid–nitric acid: (△) without $Tl^+$; (▲) 1.0 mmol $dm^{-3}$ $Tl^+$. 0.4 mol $dm^{-3}$ sulfuric acid–sodium nitrate: (□) without $Tl^+$; (■) 1.0 mmol $dm^{-3}$ $Tl^+$.

$\frac{1}{3}$ and 3 during irradiation, with $Ce^{III}$ being added prior to irradiation or introduced by pre-irradiation. The initial concentration of $Tl^+$ was 1.0 mmol $dm^{-3}$ for 0.4 mol $dm^{-3}$ sulfuric acid with nitric acid or sodium nitrate solutions and 5.0 mmol $dm^{-3}$ for nitric acid solutions. The dose rates were *ca.* 0.02–0.075 Gy $s^{-1}$ in the presence of $Tl^+$ and 0.06–0.14 Gy $s^{-1}$ in its absence. The yields of the reduction of $Ce^{IV}$ to $Ce,^{III}$ $G(-Ce^{IV})$, were calculated from the $[Ce^{IV}]$–dose curves with good linearity in the dose range studied, *i.e.* less than 330 Gy. The results are shown in Fig. 1. The radiolytic reduction of $Ce^{IV}$ to $Ce^{III}$ in 0.4 mol $dm^{-3}$ sulfuric acid has been studied extensively and established as a standard dosimeter.[14] In nitric acid and 0.4 mol $dm^{-3}$ sulfuric acid with nitric acid or sodium nitrate solutions, the yields, $G(-Ce^{IV})$, are remarkably enhanced. Addition of $Tl^+$ nearly doubles $G(-Ce^{IV})$. Our results in 0.4 mol $dm^{-3}$ sulfuric acid with nitric acid or sodium nitrate solutions are in good agreement with those reported previously[7–11] whereas the present results in nitric acid solutions are appreciably higher than those reported by Bugaenko and Roschektaer[12] and Vladimirova *et al.*[13] As shown in Fig. 1, the three systems are slightly different from each other.

## Reaction Mechanism of Radiolytic Reduction of $Ce^{IV}$ to $Ce^{III}$

The radiolysis of water generates $e^-_{aq}$, H, $H_2$, OH, $H_2O_2$ and $H^+$ as primary products and the radiolysis of nitric acid gives rise to $NO_3 + e^-_{aq}$ and $O + NO_2^-$.[1,2] Material balances were assumed for these processes. The yield, $g(e^-_{aq})$, designates the sum of pre-hydrated and hydrated electrons. The oxygen atom formed in reactions (3) and (4) has been shown to be probably in the triplet state, $O(^3P)$, which reacts with nitrate anion to yield $O_2 + NO_2^-$ by reaction (5).[2] The added metal ions, $Ce^{IV}$, $Ce^{III}$ and $Tl^+$, cannot compete for the oxygen atom owing to their low concentrations. The direct action of radiation on sulfuric acid gives rise to $SO_4^- + e^-_{aq}$,[15] which was neglected in the present study because of the small electron fraction for sulfuric acid.

$$H_2O \rightsquigarrow e^-_{aq}, H, H_2, OH, H_2O_2, H^+ \tag{1}$$

$$\begin{aligned} g_w(-H_2O) &= g_w(e^-_{aq} + H) + 2g_w(H_2) \\ &= g_w(OH) + 2g_w(H_2O_2) \end{aligned} \tag{I}$$

$$NO_3^-(HNO_3) \rightsquigarrow NO_3 + e^-_{aq}(e^-_{aq} + H^+) \tag{2}$$

$$g_{s1}(-\text{nitric acid}) = g_{s1}(NO_3) = g_{s1}(e^-_{aq}) \tag{II}$$

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

$$g_{s2}(-NO_3^-) = g_{s2}(NO_2^-) = g_{s2}(O) \tag{III}$$

$$HNO_3 \rightsquigarrow O + HNO_2 \tag{4}$$

$$g'_{s2}(-HNO_3) = g'_{s2}(HNO_2) = g'_{s2}(O) \tag{IV}$$

$$O + NO_3^- \rightarrow O_2 + NO_2^- \tag{5}$$

In the solutions containing $Ce^{IV}$ and $Ce^{III}$ without $Tl^+$, $Ce^{III}$ is oxidized by OH and $NO_3$ and $Ce^{IV}$ reduced by $HNO_2$ and $H_2O_2$ as well as by $e_p^-/e^-_{aq}$ and H *via* formation of $HNO_2$ by the following reactions [(11)–(15)].[11,16–19] Assuming that $H_2$ and $H_2O_2$ are only formed from the radiolysis of water, the yields of $G(-Ce^{IV})$ in the absence of $Tl^+$, $G_1(-Ce^{IV})$, can be expressed by eqn. (V) and the yields of oxygen $G(O_2)$ by eqn. (VI*a*) and (VI*b*), where $f_s$ and $f_w$ are the electron fractions of water and nitric acid or nitrate anion calculated from their total (inner-sphere and valence) electrons, respectively, with $f_s + f_w = 1$, and $\alpha$ is the degree of dissociation of nitric acid.

$$Ce^{III} + OH + H^+ \rightarrow Ce^{IV} + H_2O \tag{6}$$

$$OH + HNO_3 \rightarrow H_2O + NO_3 \tag{7}$$

$$Ce^{III} + NO_3 \rightarrow Ce^{IV} + NO_3^- \tag{8}$$

$$2Ce^{IV} + HNO_2 + H_2O \rightarrow 2Ce^{III} + NO_3^- + 3H^+ \tag{9}$$

$$2Ce^{IV} + H_2O_2 \rightarrow 2Ce^{III} + O_2 + 2H^+ \tag{10}$$

$$e^-_{aq} + H^+ \rightarrow H \tag{11}$$

$$e^-_{aq}(e^-_p) + NO_3^- + H_2O \rightarrow NO_2 + 2OH^- \tag{12}$$

$$H + NO_3^- \rightarrow NO_2 + OH^- \tag{13}$$

$$NO_2 + NO_2 = N_2O_4 \tag{14}$$

$$N_2O_4 + H_2O \rightarrow HNO_2 + H^+ + NO_3^- \tag{15}$$

$$\begin{aligned} G_1(-Ce^{IV}) = f_w[&g_w(e^-_{aq} + H) - g_w(OH) \\ &+ 2g_w(H_2O_2)] \\ &+ f_s[g_{s1}(e^-_{aq}) - g_{s1}(NO_3)] \\ &+ 4f_s[\alpha g_{s2}(-NO_3^-) \\ &+ (1 - \alpha)g'_{s2}(-HNO_3)] \end{aligned} \tag{V}$$

$$\begin{aligned} G(O_2) = f_w g_w(H_2O_2) + f_s[&\alpha g_{s2}(-NO_3^-) \\ &+ (1 - \alpha)g'_{s2}(-HNO_3)] \end{aligned} \tag{VIa}$$

$$G(O_2) = [G_1(-Ce^{IV}) + 2f_w g_w(H_2)]/4 \tag{VIb}$$

In the solutions containing $Ce^{IV}$ and $Ce^{III}$ with $Tl^+$, the following reactions (16)–(18) occur additionally. The yields of $G(-Ce^{IV})$ in the presence of $Tl^+$, $G_2(-Ce^{IV})$, can be expressed by eqn. (VII) and the yields of oxygen $G(O_2)$ still by eqn. (VI*a*). Thus eqn. (VIII)–(XIII) can be derived from eqn. (V) and (VII) and the material balance eqn. (I)–(IV) giving the primary yields of water radiolysis obtainable experimentally on the basis of $G_1(-Ce^{IV})$, $G_2(-Ce^{IV})$, $G(H_2)$, $g_{s1}$, $g_{s2}$, and $g'_{s2}$, where $G(H_2)$ is the observed yield of $H_2$ in the solutions.

$$OH + Tl^{+} + H^{+} \rightarrow Tl^{2+} + H_2O \quad (16)$$

$$NO_3 + Tl^{+} \rightarrow Tl^{2+} + NO_3^{-} \quad (17)$$

$$Tl^{2+} + Ce^{IV} \rightarrow Tl^{3+} + Ce^{III} \quad (18)$$

$$\begin{aligned} G_2(-Ce^{IV}) = {} & f_w\,[g_w(e_{aq}^{-} + H) + g_w(OH) \\ & + 2g_w(H_2O_2)] \\ & + f_s[g_{s1}(e_{aq}^{-}) + g_{s1}(NO_3)] \\ & + 4f_s[\alpha g_{s2}(-NO_3^{-}) \\ & + (1 - \alpha)g'_{s2}(-HNO_3)] \end{aligned} \quad (VII)$$

$$\begin{aligned} f_w\,g_w(OH) + f_s\,g_{s1}(NO_3) = {} & [G_2(-Ce^{IV}) \\ & - G_1(-Ce^{IV})]/2 \end{aligned} \quad (VIII)$$

$$\begin{aligned} g_w(OH) = {} & \{[G_2(-Ce^{IV}) - G_1(-Ce^{IV})]/2 \\ & - f_s\,g_{s1}(NO_3)\}/f_w \end{aligned} \quad (IX)$$

$$\begin{aligned} g_w(-H_2O) = {} & \{G_2(-Ce^{IV}) + 2f_w\,g_w(H_2) \\ & - 2f_s\,g_{s1}(NO_3) \\ & - 4f_s[\alpha g_{s2}(-NO_3^{-}) \\ & + (1 - \alpha)g'_{s2}(-HNO_3)]\}/(2f_w) \end{aligned} \quad (X)$$

$$g_w(e_{aq}^{-} + H) = g_w(-H_2O) - 2g_w(H_2) \quad (XI)$$

$$g_w(H_2O_2) = [g_w(-H_2O) - g_w(OH)]/2 \quad (XII)$$

$$g_w(H_2) = G(H_2)/f_w \quad (XIII)$$

## Primary Yields of Water Radiolysis

The yields of $G(H_2)$ in nitric acid and neutral sodium nitrate solutions are identical up to at least 8 mol dm$^{-3}$.[9] For the three systems investigated in the present study, the yields of $G(H_2)$ were assumed to be the same as those in nitric acid and sodium nitrate solutions. The yields of $g_{s1}$, $g_{s2}$ and $g'_{s2}$ have been evaluated as 0.50, 0.16 and 0.21 μmol J$^{-1}$ for nitric acid solutions[1,2] and were assumed to be the same for the three systems of the present study. The concentrations of molecular $HNO_3$ were neglected for 0.4 mol dm$^{-3}$ sulfuric acid–sodium nitrate solutions and were assumed to be the same as those in nitric acid solutions[20] for 0.4 mol dm$^{-3}$ sulfuric acid–nitric acid solutions. In the calculation of the electron fractions, the contribution of sulfuric acid was neglected and for 0.4 mol dm$^{-3}$ sulfuric acid–sodium nitrate solutions, the electron fractions were modified as $f_s = f(NO_3^{-})/[f(H_2O) + f(NO_3^{-})]$ and $f_w = 1 - f_s$, where $f(H_2O)$ and $f(NO_3^{-})$ are the real electron fractions of water and nitrate anion, which means that the energy absorbed by $Na^{+}$, by hypothesis, was shared by water and nitrate anion proportionally to their electron fractions. Thus we can calculate the primary yields of water radiolysis by eqn. (IX)–(XIII). The results are shown in Fig. 2–4. The decomposition of water

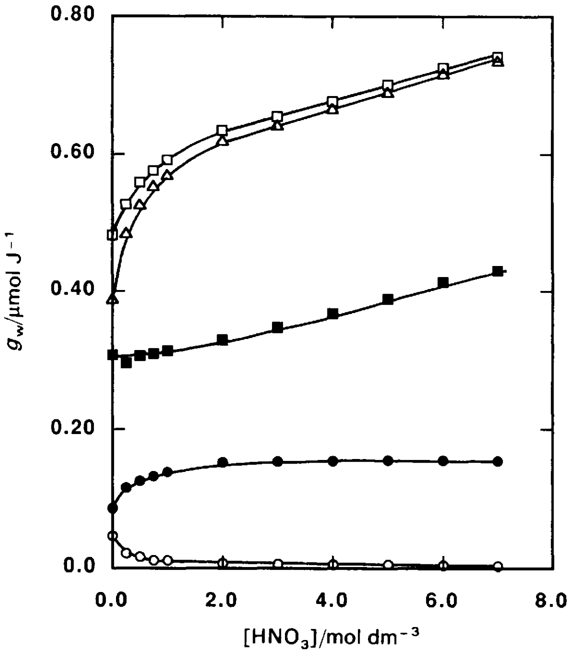

**Fig. 3** Primary yields of water radiolysis in 0.4 mol dm$^{-3}$ sulfuric acid–nitric acid solutions. $g_w(-H_2O)$ (□), $g_w(e_{aq}^{-} + H)$ (△), $g_w(OH)$ (■), $g_w(H_2O_2)$ (●) and $g_w(H_2)$ (○).

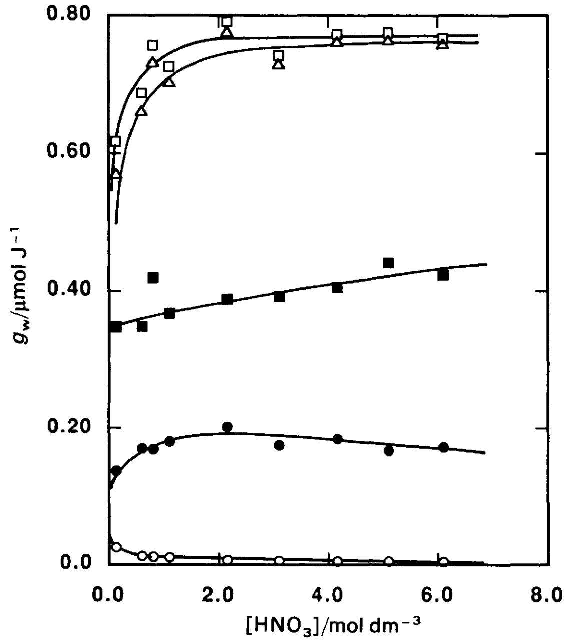

**Fig. 2** Primary yields of water radiolysis in nitric acid solutions. $g_w(-H_2O)$ (□), $g_w(e_{aq}^{-} + H)$ (△), $g_w(OH)$ (■), $g_w(H_2O_2)$ (●) and $g_w(H_2)$ (○).

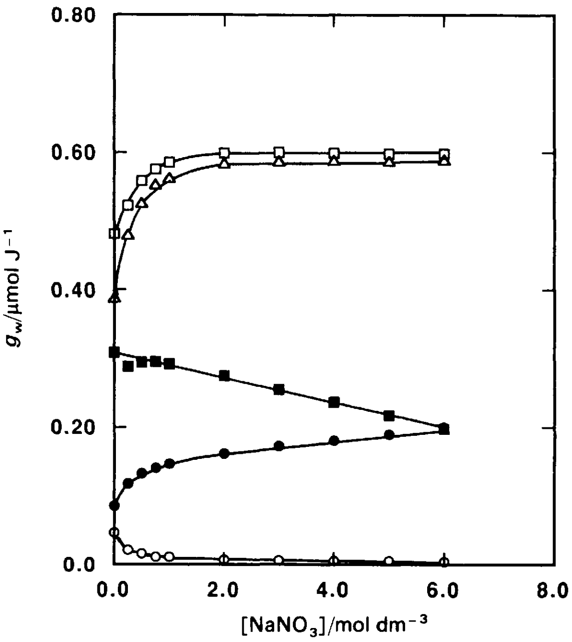

**Fig. 4** Primary yields of water radiolysis in 0.4 mol dm$^{-3}$ sulfuric acid–nitrate solutions. $g_w(-H_2O)$ (□), $g_w(e_{aq}^{-} + H)$ (△), $g_w(OH)$ (■), $g_w(H_2O_2)$ (●) and $g_w(H_2)$ (○).

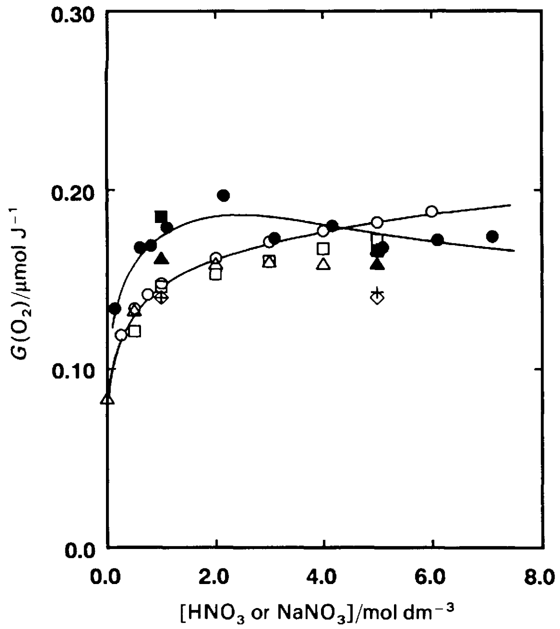

**Fig. 5** The yields of $G(O_2)$ in nitric acid and 0.4 mol dm$^{-3}$ sulfuric acid–sodium nitrate solutions containing $Ce^{IV}$ and $Ce^{III}$. Predicted $G(O_2)$ by eqn. (VI*a*) in nitric acid: (●) dose rate 0.02–0.14 Gy s$^{-1}$, this work and 0.4 mol dm$^{-3}$ sulfuric acid–sodium nitrate (○): dose rate 0.02–0.14 Gy s$^{-1}$, this work. Calculated $G(O_2)$ as $[G_1(-Ce^{IV}) + 2f_w g_w(H_2)]/4$ in nitric acid: (▲) dose rate 0.0016 Gy s$^{-1}$; (◇) dose rate 1.6 Gy s$^{-1}$, ref. 13 and 0.4 mol dm$^{-3}$ sulfuric acid–sodium nitrate (△), ref. 10. Measured $G(O_2)$ in nitric acid: (■) dose rate 0.0016 Gy s$^{-1}$; (+) dose rate 1.6 Gy s$^{-1}$, ref. 13 and 0.4 mol dm$^{-3}$ sulfuric acid + sodium nitrate (□), ref. 10.

increases rapidly with nitric acid or nitrate concentration at lower concentrations whereas it increases slowly or reaches a constant value at higher concentrations with $g_w(-H_2O)$ values as high as 0.76 μmol J$^{-1}$ in higher than *ca.* 1 mol dm$^{-3}$ nitric acid solutions. Apparently the three systems differ from each other, presumably, owing to the influence of acidity on spur reactions, the nuances of which are rather difficult to understand quantitatively at present if possible. A rational description might be as follows: the scavenging of $e_p^-/e_{aq}^-$ by $NO_3^-$/$HNO_3$ leads to the increases in $g_w(e_{aq}^- + H)$ and $g_w(-H_2O)$ because of the lower reactivities of the $NO_2$ species formed and its precursors whereas the competition for $e_{aq}^-$ (but not $e_p^-$) by $H^+$ suppresses this effect due to the high reactivity of the H atom formed. The scavenging of OH by undissociated $HNO_3$ leads to increases in $g_w(OH)$ and $g_w(-H_2O)$ owing to the lower reactivity of the $NO_3$ radical formed. Thus it is expected that the increases in $g_w(e_{aq}^- + H)$, $g_w(OH)$ and $g_w(-H_2O)$ should be greatest in pure nitric acid solutions and least in the 0.4 mol dm$^{-3}$ sulfuric acid–sodium nitrate solutions, which is in general agreement with the experiment results.

The formation of $O_2$ has been investigated and the values of $G(O_2)$ reported for nitric acid and 0.4 mol dm$^{-3}$ sulfuric acid–sodium nitrate solutions.[10,13] The values of $G(O_2)$ calculated from eqn. (VI*a*) on the basis of the primary yields evaluated in the present study are compared with the experimentally measured values of $G(O_2)$ as shown in Fig. 5, which are in good agreement for 0.4 mol dm$^{-3}$ sulfuric acid–sodium nitrate solutions[10] and for nitric acid solutions at lower dose rate under more or less similar experimental conditions to the present study.[13] The lower $G(O_2)$ values in nitric acid solutions at higher dose rate (10–100 times higher than those in the present study)[13] are presumably due to the reaction of $H_2O_2$ with $HNO_2$[21] because of the higher dose rate and lower initial concentration of $[Ce^{IV}]_0 = 0.1$ mmol dm$^{-3}$. The values of $G(O_2)$ can also be obtained from eqn. (VI*b*) which is valid even when reaction (19) occurs. As shown also in Fig. 5, the values of $G(O_2)$ derived as $[G_1(-Ce^{IV}) + 2f_w g_w(H_2)]/4$ are in good agreement with the experimental values of $G(O_2)$ under various conditions for nitric acid solutions[13] and 0.4 mol dm$^{-3}$ sulfuric acid–sodium nitrate solutions[10] even when eqn. (VI*a*) is not applicable. These facts are in quantitive agreement with the present reaction mechanism and the derived primary yields.

$$HNO_2 + H_2O_2 \rightarrow H_2O + NO_3^- + 3H^+ \qquad (19)$$

Attempts have been made to evaluate the yields of $G(H_2O_2)$ in nitric acid solutions.[11,22] In 0.4 mol dm$^{-3}$ sulfuric acid–5.0 mol dm$^{-3}$ sodium nitrate solutions, the value of $G(H_2O_2)$ has been deduced as 0.12 μmol J$^{-1}$,[11] in reasonable agreement with the value of $G(H_2O_2) = f_w g_w(H_2O_2) = 0.14$ μmol J$^{-1}$ derived in the present study. In nitric acid solutions containing sulfanilamide as a $HNO_2$ scavenger, $G(H_2O_2)$ has been obtained as 0.083 (0.05), 0.084 (0.1), 0.11 (0.5), and 0.114 (1.0 mol dm$^{-3}$ nitric acid) μmol J$^{-1}$,[22] increasing with nitric acid concentration, which is fairly consistent with the trend predicted in the present study. Since sulfanilamide is a scavenger of OH and $NO_3$,[1] the system containing sulfanilaide is presumably different from that of the present study, which may give different $G(H_2O_2)$ values.

The mechanism of water radiolysis has been established and the primary yields are well documented. In 0.4 mol dm$^{-3}$ sulfuric acid solutions, $g_w(e_{aq}^- + H) = 0.383$, $g_w(H_2) = 0.041$, $g_w(OH) = 0.30$, $g_w(H_2O_2) = 0.083$ and $g_w(-H_2O) = 0.466$ μmol J$^{-1}$ as measured by the Fricke dosimeter. In the pulse radiolysis studies, the initial value of $g_w(OH)$ was found to be 0.611 μmol J$^{-1}$ at 200 ps,[23] and that of $g_w(e_{aq}^-)$ to be 0.50 μmol J$^{-1}$ at 30 ps[24] and 0.48 μmol J$^{-1}$ at 100 ps.[25] These initial yields have been generally accepted in computer simulation of spur reactions.[26] The yield of water decomposition in nitric acid solutions is as high as 0.76 μmol J$^{-1}$, which may give considerably higher initial yields for OH and $e_{aq}^-$, presumably, corresponding to earlier times. The yield of water decomposition (initial or at $10^{-12}$–$10^{-11}$ s) has been obtained as 0.90,[27] 0.71,[28] *ca.* 0.8,[29] and 0.70[30] μmol J$^{-1}$ by therotical calculation, which is supported by the present results.

This work was supported in part by a Grant-in-Aid for Scientific Research (No. B-04453163), from the Ministry of Education, Science and Culture of the Japanese Government.

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*Paper* 3/05139K; *Received* 25*th August*, 1993