

Reduction Potential of the Nitrate Radical in Aqueous Solution

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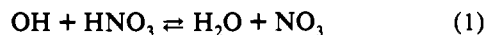
Numerous studies have been carried out on the reactions of the nitrate radical (NO_3) in the gas and liquid phases.^{2,3} In the liquid phase, the nitrate radical not only reacts by abstraction or addition but also engages in electron transfer.² The reduction potential of the nitrate radical in aqueous solution, $E^\circ(\text{NO}_3/\text{NO}_3^-)$, has been estimated as 2.3,⁴ 1.9,⁵ 2.28,⁶ and 2.49 V⁷ from the gas-phase $\Delta G^\circ_f(\text{NO}_3)$ value combined with the estimated hydration free energy of the nitrate radical. On the basis of the reaction rate constants of the nitrate radical, the value of $E^\circ(\text{NO}_3/\text{NO}_3^-)$ has been estimated in the range 2.3–2.7 V.⁸ An experimental measurement of the reduction potential of the nitrate radical is reported here.

Experimental Section

Electron pulses of 100 ns and 28 MeV from a linear accelerator at the Nuclear Engineering Research Laboratory, University of Tokyo, were used. Details of the pulse radiolysis system have been described elsewhere.^{9,10} The absorbance of the nitrate radical was followed at 640 nm. For dosimetry, a 10 mM KSCN aqueous solution saturated with N_2O was used with $G_\epsilon(472 \text{ nm}) = 46\,400$ (molecule/100 eV) $\text{M}^{-1} \text{cm}^{-1}$ for the radical anion $(\text{SCN})_2^-$.¹¹ Absorbed doses in nitric acid solutions were corrected for their electron densities. Chemicals are of the highest available purity and were used as received. All experiments were carried out at room temperature (around 20 °C) in aerated solutions unless otherwise stated.

Results and Discussion

Kinetic Treatment. In the pulse radiolysis of nitric acid solutions, the hydroxyl radical is converted to the nitrate radical until equilibrium 1 is established.¹⁰ The formation rate constant



$$k_{\text{obs}} = k_f[\text{H}_2\text{O}] + k_r[\text{HNO}_3] \quad (2a)$$

of the nitrate radical can be described by eq 2a when the hydroxyl and nitrate radicals do not decay during the establishment of equilibrium 1, where k_f and k_r ($\text{M}^{-1} \text{s}^{-1}$) are the forward and

Table I. Reaction Scheme for Nitric Acid Solutions^a

reaction	no.	$k/\text{M}^{-1} \text{s}^{-1}$	ref
$\text{OH} + \text{HNO}_3 \rightarrow \text{NO}_3 + \text{H}_2\text{O}$	1f	5.3×10^7	see text
$\text{NO}_3 + \text{H}_2\text{O} \rightarrow \text{OH} + \text{HNO}_3$	1r	5.3×10^5	see text
$e_{\text{aq}}^- + \text{H}^+ \rightarrow \text{H}$	3	2.3×10^{10}	12
$e_{\text{aq}}^- + \text{NO}_3^- \xrightarrow{2\text{H}^+} \text{NO}_2 + \text{H}_2\text{O}$	4	9.7×10^9	12
$\text{H} + \text{NO}_3^- \xrightarrow{\text{H}^+} \text{NO}_2 + \text{H}_2\text{O}$	5	1×10^7	13
$\text{H} + \text{O}_2 \rightarrow \text{HO}_2$	6	2.1×10^{10}	12
$\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$	7	7.9×10^9	12
$\text{OH} + \text{NO}_2 \rightarrow \text{NO}_3^- + \text{H}^+$	8	1.3×10^9	2
$\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2$	9	5.5×10^9	12
$\text{NO}_3 + \text{NO}_2 \rightarrow \text{N}_2\text{O}_5$	10	1.7×10^9	10
$\text{NO}_3 + \text{HO}_2 \rightarrow \text{NO}_3^- + \text{H}^+ + \text{O}_2$	11	3×10^9	14
$\text{NO}_2 + \text{NO}_2 \rightarrow \text{N}_2\text{O}_4$	12	4.5×10^8	15
$\text{N}_2\text{O}_4 \rightarrow \text{NO}_2 + \text{NO}_2$	13	6.8×10^3	15

^a $G(e_{\text{aq}}^-) = 3.5$, $G(\text{H}) = 0.8$, and $G(\text{OH}) = 3.2$ molecule/100 eV.

Table II. k_{obs} and Decay Percentage of $\text{OH} + \text{NO}_3$ in Nitric Acid Solutions

$[\text{HNO}_3]/\text{M}$	$k_{\text{obs}}/10^6 \text{ s}^{-1}$	$t_{1/2}^a/10^{-6} \text{ s}$	dp ^b /%
0.2	0.246	2.8	38
0.3	0.391	1.8	24
0.5	0.961	0.7	8.7
0.6	1.17	0.6	6.6
0.7	1.40	0.5	5.0
1.0	2.54	0.27	2.3
1.5	5.33	0.13	0.9

^a Half-lives of NO_3 formation. $t_{1/2} = (\ln 2)/k_{\text{obs}}$. ^b Decay percentage of OH and NO_3 defined as $\text{dp} = (1 - [\text{OH} + \text{NO}_3]_t/[\text{OH} + \text{NO}_3]_0) \times 100$ at $t = 4t_{1/2}$. Dose/pulse = 11 Gy/pulse for the dosimetry solution.

reverse rate constants of equilibrium 1 and k_{obs} (s^{-1}) is the observed pseudo-first-order formation rate constant of the nitrate radical.

OH– NO_3 Equilibrium. In the pulse radiolysis of nitric acid solutions, the yields of the nitrate radical increase rapidly with nitric acid concentration in 0.2–0.5 M nitric acid solutions while only slightly in higher than 0.5 M nitric acid solutions,¹⁰ suggesting that the establishment of equilibrium 1 is fast in higher than 0.5 M nitric acid solutions, during which the decay of the hydroxyl and nitrate radicals is not significant. On the basis of the reaction scheme shown in Table I, the decay of the hydroxyl and nitrate radicals was roughly estimated as shown in Table II, confirming the above conclusion. All calculations were carried out by using FACSIMILE¹⁶ with the primary yields shown in Table I. The concentrations of oxygen are in the range of 0.23–0.26 mM for 0.2–1.5 M nitric acid.¹⁷ No accurate primary yields are available for nitric acid solutions. In 0.6 M HNO_3 , $G(\text{OH}) = 3.2^{10}$ and $G(\text{H}_2) = 0.15$.¹⁸ The decrease in $G(\text{H}_2)$ is due to the scavenging of e_{aq}^- by NO_3^- , and thus $G(e_{\text{aq}}^- + \text{H})$ increases. A value of $G(e_{\text{aq}}^- + \text{H}) = 4.3$ was assumed here with $G(e_{\text{aq}}^-) = 3.5$ and $G(\text{H}) = 0.8$. These primary yields were used in all calculations. We are only interested in the rough estimation of the decay of the hydroxyl and nitrate radicals during the approach to equilibrium 1. The uncertainties in the primary yields do not appreciably affect the calculated decay percentage of the hydroxyl and nitrate radicals.

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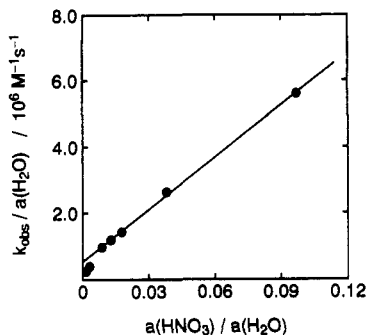


Figure 1. $k_{\text{obs}}/a(\text{H}_2\text{O})$ vs $a(\text{HNO}_3)/a(\text{H}_2\text{O})$ for 0.2–1.5 M HNO_3 solutions.

Thus, the temporal profiles of the nitrate radical formation were fitted to first-order kinetics by a nonlinear least-squares method to yield k_{obs} as shown in Table II. The formation of the nitrate radical can be described well by first-order kinetics for 0.5–1.5 M nitric acid solutions whereas inadequately for 0.2 and 0.3 M nitric acid solutions in which the decay of the hydroxyl and nitrate radicals during the establishment of equilibrium 1 is significant.

Equation 2b is obtained from eq 2a by using activity instead of concentration, where $a(\text{HNO}_3)$ and $a(\text{H}_2\text{O})$ are the activities

$$k_{\text{obs}}/a(\text{H}_2\text{O}) = k_r + k_f a(\text{HNO}_3)/a(\text{H}_2\text{O}) \quad (2b)$$

of molecular HNO_3 and H_2O , respectively, which are obtainable from ref 19. A plot of $k_{\text{obs}}/a(\text{H}_2\text{O})$ vs $a(\text{HNO}_3)/a(\text{H}_2\text{O})$ is shown in Figure 1, giving $k_r = 5.3 \times 10^5$ and $k_f = 5.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. The value of k_f has been previously evaluated as $1.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.¹⁰ The discrepancy is mainly due to different data on the degree of dissociation of nitric acid that have been used and partially due to the use of activity instead of concentration.

Reduction Potential of NO_3^- . The equilibrium constant $K_1 = k_f/k_r = 1.0 \times 10^2$. Thus, the difference between $E^\circ(\text{NO}_3, \text{H}^+/\text{HNO}_3)$ and $E^\circ(\text{OH}, \text{H}^+/\text{H}_2\text{O})$ is 0.118 V, giving $E^\circ(\text{NO}_3, \text{H}^+/\text{HNO}_3) = 2.60 \text{ V}$ on the basis of $E^\circ(\text{OH}, \text{H}^+/\text{H}_2\text{O}) = 2.72 \text{ V}$.^{20,21} For nitric acid in aqueous solutions, $K_a = 15.3 \text{ M}$;¹⁹ thus, $E^\circ(\text{NO}_3/\text{NO}_3^-) = 2.67 \text{ V}$.

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