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triplet nature of the initial geminate radical pair may prevent immediate disproportionation to regenerate starting materials and, thus, allow some separation of the radicals. Alternately, interaction of the radicals (in particular the ketyl radical) with the surface may lead to sufficient stabilization to inhibit back-reaction. Further studies of radical pairs on silica that are directed at sorting out some of these questions are in progress.

In conclusion, the present results provide direct evidence for hydrogen abstraction reactions for triplet benzophenone adsorbed on silica. Both static and dynamic quenching mechanisms have been observed, and kinetic parameters for the latter have been measured. These hydrogen-transfer reactions are over an order of magnitude slower than energy transfer to naphthalene. The results also demonstrate the potential of diffuse reflectance techniques for obtaining kinetic information for reactions on surfaces and for obtaining detailed information concerning the intermediates involved in bimolecular reactions.

Acknowledgment. We thank Mr. S. Sugamori and Mr. G. Charette for technical assistance.

Pulse Radiolysis Study of Aqueous Nitric Acid Solutions. Formation Mechanism, Yield, and Reactivity of NO_3 Radical

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A pulse radiolysis study of aqueous nitric acid and nitrate solutions has been carried out. The formation kinetics of NO_3 radical was followed with nanosecond time resolution. Two formation processes of NO_3 in nitric acid solutions were directly demonstrated: a fast one completed during the electron pulse and a slow one occurring in a microsecond time range. In nitrate solutions, only the fast formation process was observed. The slow formation process in nitric acid solutions was confirmed to be the reaction of OH radicals with undissociated nitric acid molecules, $OH + HNO_3 \rightarrow H_2O + NO_3$, with a rate constant of $(1.4 \pm 0.1) \times 10^8\ M^{-1}\ s^{-1}$. The fast formation process is most probably the direct action of radiation on nitrate anion or nitric acid: $NO_3^- \rightsquigarrow e^- + NO_3$ or $HNO_3 \rightsquigarrow HNO_3^+ + e^- \rightarrow NO_3 + H^+ + e^-$. The molar absorption coefficient of NO_3 was evaluated as $1300 \pm 100\ M^{-1}\ cm^{-1}$ at 640 nm. On the basis of this result, G values of NO_3 were evaluated in nitric acid, lithium nitrate, and sodium nitrate solutions. The main decay reaction of NO_3 was proposed to be $NO_3 + NO_2 \rightarrow N_2O_5$ in nitric acid solutions and its rate constant was evaluated as $(1.7 \pm 0.3) \times 10^9\ M^{-1}\ s^{-1}$. Rate constants of reactions of NO_3 with radiolytic products and some other compounds were obtained.

Introduction

Concentrated nitric acid solutions have been widely used in the nuclear industry, especially in spent fuel reprocessing. It is indispensable to understand the radiolysis of nitric acid solutions from the viewpoint of understanding and controlling the degradation and nitration of the solvents used to recover uranium and plutonium, the change of valence states of the actinides, and the corrosion of the containers used under strong radiation fields.[1] Radiolysis of nitric acid solutions has been studied by many investigators.[2] In pulse radiolysis studies, nitrate (NO_3) radical has been found as one of the most important intermediates. Numerous investigations have been carried out on its formation mechanism, yield, and reactivity.[3-13] Three processes have been proposed for the production of NO_3 radical: reaction of OH radicals with undissociated nitric acid molecules,[4,6,7] direct action of radiation on nitrate anions,[3,5,6] and reaction of nitrate anions with H_2O^+.[9,13,14] Many questions, however, still remain open in explaining the formation mechanism of NO_3 in the radiolysis of nitric acid and nitrate solutions. The yields of NO_3 in the radiolysis of nitric acid solutions have been evaluated by Pikaev et al.[6] and Kozlowska-Milner et al.[7] up to anhydrous nitric acid. The exceptionally high yields of NO_3 have not yet been satisfactorily explained. Recent results[15] show that the molar absorption coefficient they used is significantly underestimated. Due to its importance in atmospheric chemistry, the reactivity of NO_3 has been studied intensively in the gas phase[16] as well as in the liquid phase by photolysis and pulse radiolysis.[8,11,12] However, there is no report on its reactions with radiolytic products of nitric acid solutions such as H_2O_2 and HNO_2, which is important for understanding the radiolytic processes. Besides the formation mechanism, the decay mechanism of NO_3 has also not been clearly understood yet.

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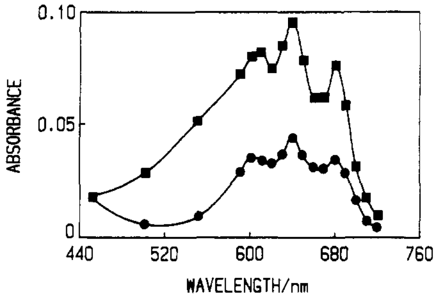

Figure 1. Transient spectra from 6 M HNO_3 (■) and 6 M $NaNO_3$ (●) solutions following 100-ns electron pulses.

All these justify the purposes of this study: (1) to follow the formation kinetics of NO_3 with nanosecond time resolution so as to elucidate the exact formation mechanism, (2) to determine the molar absorption coefficient (ϵ) and thus to evaluate the G values of NO_3, and (3) to study the decay kinetics of NO_3 and the reactions of NO_3 with compounds of interest.

Experimental Section

Electron pulses of 10–100 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 already been reported elsewhere.[17] A Xe flash lamp was normally used as the light source, and sometimes, a He–Ne laser (633 nm) was used. The analyzing light passed through a 5-cm optical cell and was reflected through the cell again; thus, an optical path of 10 cm was obtained so as to get higher sensitivity. In nanosecond-scale time-resolved experiments, a 2-cm optical cell was used. For dosimetry, 10 mM KSCN aqueous solution saturated with N_2O was employed with $G = 6.1$ and $\epsilon(472\ \text{nm}) = 7580\ M^{-1}\ cm^{-1}$ for $(SCN)_2^{-}$.[18] The unit of the G values is molecule/100 eV in this paper. The absorbed energy in concentrated solution was corrected for the electron density of the solution. Nitric acid, sodium nitrate, lithium nitrate, and other chemicals from Wako Chemical Co., Ltd. were used as received. Samples were prepared with doubly distilled water just before irradiation. All experiments were carried out at room temperature (around 18 °C) in aerated solutions if not otherwise specified.

Results and Discussion

Absorption Spectrum of NO_3. When nitric acid solutions were irradiated, a characteristic absorption spectrum showing peaks at 600, 640, and 675 nm was observed as shown in Figure 1, which is clearly very similar to the spectrum of NO_3 radical reported earlier,[3,4,8] confirming that the observed species is NO_3 radical. The absorption spectra are the same in 1 and 6 M nitric acid solutions. Purging the solutions with Ar to replace O_2 has no measurable effect on the absorbance of NO_3. Similar absorption spectra were also obtained in lithium nitrate and sodium nitrate solutions (see Figure 1). The absorption spectra are much broadened compared with the spectrum of NO_3 in the gas phase.[19]

Formation Kinetics of NO_3. Following a 100-ns electron pulse, the buildup of NO_3 can easily be seen in low-concentration nitric acid solutions. Figure 2 shows the temporal profile of the absorbance at 640 nm in 0.5 M nitric acid. The formation rate of NO_3 increases with increasing nitric acid concentration. The maximum absorbance of NO_3 increases rapidly with nitric acid concentration up to 1 M, whereas it increases gradually above 1 M (see Figure 2). In lithium nitrate and sodium nitrate solutions, the formation of NO_3 occurs completely during the electron pulse at all concentrations studied and its absorbance is much smaller. These results are consistent with those previous reports.[3-5]

To get a deeper insight into the formation processes, the absorbance was followed at 640 nm with nanosecond time resolution in both nitric acid and sodium nitrate solutions. The results with 3 M nitric acid and 6 M sodium nitrate are shown in Figure 3, together with the results when 0.1 M ethanol was added to both solutions. It is clear that in nitric acid solutions, NO_3 is formed from two processes: a fast one completed during the electron pulse, which is not affected by addition of ethanol, and a slow one building up on a microsecond time scale, which can be depressed by ethanol addition. The depressing extent depends on both nitric acid and scavenger concentrations. In sodium nitrate solutions, only the fast formation process was observed, similarly not affected by addition of ethanol. From these results, it is evident that the fast and slow formation processes in nitric acid solutions have different precursors, indicating two different formation processes.

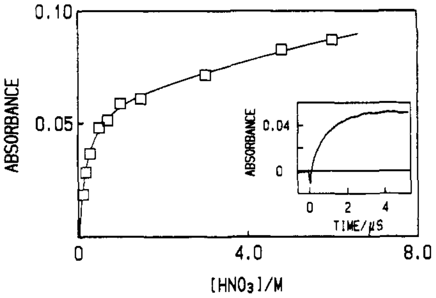

Figure 2. Maximum absorbance of NO_3 radical as a function of nitric acid concentration (640 nm). Inset: Temporal profile of NO_3 formation in 0.5 M HNO_3 (640 nm).

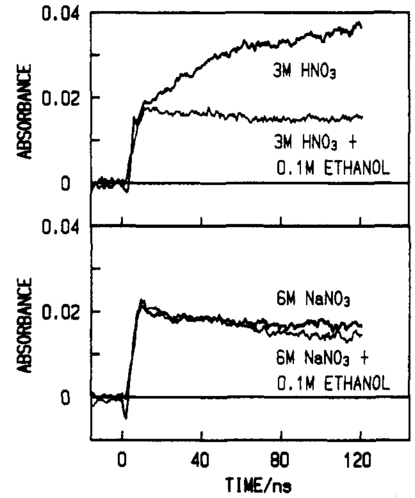

Figure 3. Formation behaviors of NO_3 radical in 3 M HNO_3 and 6 M $NaNO_3$ solutions in the presence and absence of 0.1 M ethanol (640 nm, 10-ns electron pulse).

Mechanism of the Slow Formation Process of NO_3. To verify the precursor (X) of the slow formation process in nitric acid solutions, the formation kinetics of NO_3 was studied in 0.6 M nitric acid with addition of radical scavengers. Under all conditions investigated, the experimental data can be fitted to first-order formation kinetics. The corresponding formation rates (R) expressed by eq 4 according to reactions 1–3, were evaluated.

$$X + NO_3^- \text{ or } HNO_3 \rightarrow NO_3 \qquad k_1[NO_3^- \text{ or } HNO_3] \tag{1}$$

$$X + \text{scavenger} \rightarrow S' \qquad k_2[S] \tag{2}$$

$$X + \text{other species} \rightarrow P \qquad R_0 \tag{3}$$

$$R = R_0 + k_1[NO_3^- \text{ or } HNO_3] + k_2[S] \tag{4}$$

Rate constants k_2 were evaluated by changing scavenger concentrations (0.1–1 mM). Under the conditions of this study, reactions of NO_3 with scavengers during the formation of NO_3 are negligible except for the case of KSCN. Since NO_3 reacts with SCN^- with a rate constant of $2 \times 10^9\ M^{-1}\ s^{-1}$ (see Table II), low concentrations of SCN^- (around 0.1 mM) were employed. Under this condition, the formation half-life of NO_3 is around 10 times smaller than its decay half-life through reaction with

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TABLE I: Rate Constants of Scavengers with Precursor, OH, and H (M^{-1} s^{-1})

	k_2		
scavenger	precursor, this work	OH[20]	H[20]
ethanol	2.0×10^9	1.9×10^9	1.7×10^7
hydroquinone	4.9×10^9	$(0.52-2.1) \times 10^{10}$	1.3×10^9
p-nitroaniline	1.3×10^{10}	1.4×10^{10}	2.0×10^9
KSCN	1.2×10^{10}	1.1×10^{10}	2.3×10^8
sulfanilamide	5.4×10^9	$(1.6-2.2) \times 10^9$	

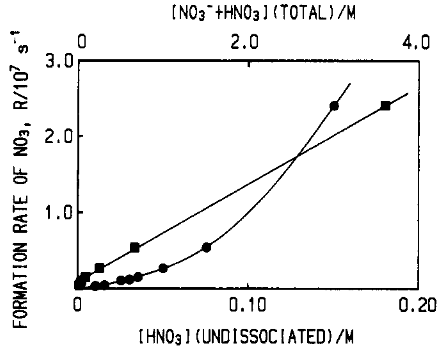

Figure 4. Dependence of first-order formation rate of NO_3 on undissociated nitric acid (■) and total nitric acid (●) concentrations.

SCN^-. The absorbance of $(SCN)_2^-$ at 640 nm is also not significant during the formation of NO_3. So, k_2 was evaluated for KSCN likewise without correction for these effects. The results are shown in Table I. The values of k_2 are in agreement with the rate constants of these scavengers with OH radical, confirming that the precursor is OH radical. Hydrated electrons and H radicals react with NO_3^- and/or H^+ to yield NO_2.[20,21] They cannot be the precursors of NO_3.

The slow formation process cannot be observed in nitrate solutions, suggesting that only the undissociated HNO_3 molecule (which only exists in nitric acid solutions) reacts with OH radical as proposed earlier.[4,6,7] To clarify this point, the formation kinetics of NO_3 was studied in 0.2–3 M nitric acid solutions. The observed formation rates (R), expressed by eq 4 with [S] = 0, were evaluated by fitting the experimental data to first-order formation kinetics. As shown in Figure 4, R is a linear function of undissociated nitric acid concentration. The concentrations of undissociated nitric acid were calculated from the degree of dissociation (25 °C) determined by Redlich et al. by means of NMR spectroscopy.[22] A plot of R as a function of total nitric acid concentration gives a curved line as also shown in Figure 4. From these results, we conclude that the reaction partner is the undissociated nitric acid molecule. Thus, reaction 5 is responsible

$$OH + HNO_3 \rightarrow H_2O + NO_3 \quad (5)$$

for the slow formation process and the rate constant (k_5) was evaluated as $(1.4 \pm 0.1) \times 10^8$ M^{-1} s^{-1}.

Yield of NO_3. No evaluation of the molar absorption coefficient (ϵ) has been reported for NO_3 in the liquid phase to the present. In photolysis of ceric nitrate/nitric acid solutions, $\epsilon\phi$ (at 635 nm, ϕ is the quantum yield) has been reported to be 250 and 480 M^{-1} cm^{-1} by Martin et al.[23,24] and 830 M^{-1} cm^{-1} by Wine et al.[15]

In pulse radiolysis studies, no attempt has been made to evaluate the ϵ value because of insufficient understanding of its formation mechanism. In this study, ϵ is evaluated as follows. The absorption of $(SCN)_2^-$ was followed at 472 nm in aerated 0.6 M nitric acid solution with addition of 1 mM KSCN. Under this condition, OH radical from radiolysis of water is totally converted to $(SCN)_2^-$ directly or via formation of NO_3. A hydrated electron is scavenged by H^+ and NO_3^-. Reaction of H with SCN^- is completely depressed by O_2 and NO_3^-,[20,25] and reactions of HO_2 and NO_2 thus formed with SCN^- are less probable because of their lower reduction potential values than that of SCN radical.[26] Since the direct action of radiation on nitric acid is negligible, the yield of OH radicals in 0.6 M nitric acid solution was evaluated as 3.16 ± 0.1 based on $\epsilon(472 \text{ nm}) = 7580 \pm 80$ M^{-1} cm^{-1} for $(SCN)_2^-$.[18] In aerated 0.6 M nitric acid solution without KSCN, not all OH radicals are converted to NO_3 radicals. Considering reactions 1 and 3, we evaluated R_0 from the absorbance data shown in Figure 2 (0.2–1 M HNO_3, fast formation process neglected) to be 9.2×10^4 s^{-1}. Thus, the ratio for conversion of OH radical to NO_3 radical was calculated by $(R - R_0)/R$ (R is defined by eq 4), to be 92%. From these results, ϵ(640 nm) of NO_3 was evaluated as 1300 ± 100 M^{-1} cm^{-1}.

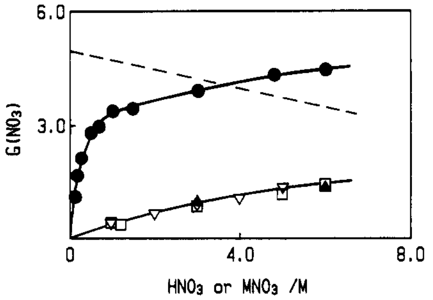

Figure 5. Dependence of $G(NO_3)$ on nitric acid and nitrate concentrations (640 nm): total (●) and fast formation process (▲) yields in HNO_3 solutions; fast formation process yields in $LiNO_3$ (▽) and $NaNO_3$ (□) solutions; primary cation yield of water, $f(H_2O)G(H_2O^+)$ ($G(H_2O^+) = 5$), in HNO_3 solution (- - -).

Similar experiments were also carried out by using 1 mM and 10 mM hydroquinone instead of 1 mM KSCN in 0.6 M nitric acid solution. The solutions were purged with Ar to replace O_2. The absorbance was followed at 415 nm. Similar results were obtained for solutions containing both 1 and 10 mM hydroquinone. $G(OH) = 2.7 \pm 0.2$ based on $\epsilon(415 \text{ nm}) = 5500$ M^{-1} cm^{-1} for the benzosemiquinone radical formed from the OH adduct of hydroquinone.[27] The value of ϵ(640 nm) was obtained as 1560 ± 150M^{-1} cm^{-1} for NO_3. There is no obvious reason for the discrepancy between the two methods. The value $\epsilon(640 \text{ nm}) = 1300 \pm 100$ M^{-1} cm^{-1} is preferred on considering the more reliable ϵ value for $(SCN)_2^-$ and the better understanding of the reactions in 0.6 M nitric acid/1 mM KSCN solution.

Recently, Wine et al.[15] reported $\epsilon(SO_4^-, 443 \text{ nm})/\epsilon(NO_3, 635 \text{ nm}) = 1.29 \pm 0.15$ and McElroy[28] reported $\epsilon(SO_4^-, 450 \text{ nm}) = 1600 \pm 100 M^{-1}$ cm^{-1}. Since $\epsilon(SO_4^-, 443 \text{ nm}) \simeq \epsilon(SO_4^-, 450 \text{ nm})$ and $\epsilon(NO_3, 635 \text{ nm}) \simeq \epsilon(NO_3, 640 \text{ nm})$, $\epsilon(NO_3, 640 \text{ nm})$ is calculated to be 1240 M^{-1} cm^{-1}, which is in fair agreement with our evaluation. The spectrum of NO_3 in the gas phase has been intensively studied recently. By equating the integrated cross section (σ) over the 25000–14500 cm^{-1} (400–690 nm) region of the gas-phase spectrum to the areas of the spectra shown in Figure 1, ϵ(640 nm, liquid phase) was calculated to be 1300 ± 300 M^{-1} cm^{-1} by taking σ(661.9 nm) to be 2×10^{-17} cm^2 $molecule^{-1}$ for the gas-phase spectrum.[19] This result is consistent with ours.

Figure 5 shows the G values of NO_3 in nitric acid, sodium nitrate, and lithium nitrate solutions. The G values of the fast and slow formation processes in nitric acid solutions were evaluated separately by a competition method as follows.

In the presence of the OH scavenger, the yield of NO_3 from the slow formation process is depressed, while that from the fast formation process remains unaffected. In higher than 1 M nitric acid solutions, reaction 3 does not proceed appreciably. Thus, eq 6 is derived from reactions 2 and 5. When [S] = 0, eq 7 is

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$$G_s = G(f) + G(s)\{k_5[HNO_3]/(k_2[S] + k_5[HNO_3])\} \quad (6)$$

$$G_0 = G(f) + G(s) \quad (7)$$

$$1/(G_0 - G_s) = 1/G(s) + k_5[HNO_3]/\{G(s)k_2[S]\} \quad (8)$$

obtained. Equation 8 is derived from eqs 6 and 7 and was applied to the experimental data. $G(s)$ and $G(f)$ are the scavengable and unscavengable yields of NO_3, representing the yields of the slow and fast formation processes, respectively, in nitric acid solutions without scavenger. G_0 and G_s are the total yields of NO_3 in nitric acid solutions in the absence and presence of OH scavenger.

In 3 M nitric acid solution with *t*-butyl alcohol as scavenger, $G(s) = 3.1$, $G(f) = 0.93$, and $k_5 = 1.3 \times 10^8$ M^{-1} s^{-1} based on k(OH + *t*-butyl alcohol) = 6.0×10^8 M^{-1} s^{-1}.[20] In 6 M nitric acid solution with 2-propanol as scavenger, $G(s) = 3.2$, $G(f) = 1.4$, and $k_5 = 1.3 \times 10^8$ M^{-1} s^{-1} based on k(OH + 2-propanol) = 2.3×10^9 M^{-1} s^{-1}.[29]

As shown in Figure 5, the G values of the fast formation process in nitric acid solutions are in good agreement with the yields of NO_3 in nitrate solutions at the same concentrations. The change of cations has no obvious effect on G values probably because their electron fractions are relatively small. On the basis of the previous results, we conclude that the fast formation processes of NO_3 are the same in nitric acid and nitrate solutions in the concentration range studied. The rate constants of reaction 5 obtained here are consistent with that evaluated before in lower concentration solutions.

Mechanism of the Fast Formation Process of NO_3. The production of NO_3 in nitrate solutions is only from the fast formation process. To explain the formation mechanism, two proposals have been put forward. One is the direct action of radiation on nitrate anion.[3,5,6] The alternative explanation is "dry hole (H_2O^+)" trapping by nitrate anion.[9,13,14]

According to the "direct action" mechanism, assuming arbitrarily that NO_3 may originate from energy deposited either in water or in nitrate anion, eq 9 is derived, where $f(H_2O)$ and

$$G(NO_3)/f(H_2O) = G(H_2O) + G(NO_3^-)f(NO_3^-)/f(H_2O) \quad (9)$$

$f(NO_3^-)$ are the electron fractions of water and nitrate anion, while $G(H_2O)$ and $G(NO_3^-)$ are the yields of the species which then form NO_3 from water and nitrate anion, respectively.[3]

The yields of NO_3 for the fast formation process in lithium nitrate, sodium nitrate, and nitric acid solutions can be fitted to eq 9 with $G(NO_3^-) = 4.8$ and $G(H_2O) \simeq 0$.

Alternatively, similar to the proposal of Hamill et al.,[30,31] σ_1 and σ_2 are arbitrarily designated as the probabilities of dry hole trapping by nitrate anion (reaction 10) and water (reaction 11).

$$H_2O^+ + NO_3^- \rightarrow H_2O + NO_3 \qquad \sigma_1 \quad (10)$$

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH \qquad \sigma_2 \quad (11)$$

$$G(NO_3) = f(H_2O)G(H_2O^+)\sigma_1[NO_3^-]/(\sigma_1[NO_3^-] + \sigma_2[H_2O]) \quad (12)$$

Equation 12 is obtained, where $f(H_2O)$ and $G(H_2O^+)$ are the electron fraction of water in solution and the primary cation yield of water, respectively.

Suppose that the fast formation process is only initiated by dry hole trapping; the yields of NO_3 of the fast formation process in lithium nitrate, sodium nitrate, and nitric acid solutions can then be fitted to eq 12, giving $G(H_2O^+) \simeq 5$ and $\sigma_1/\sigma_2 \simeq 4.5$

Numerically, the experimental results can be fitted to the two extreme cases. However, as shown in Figure 5, the total yields of NO_3 in nitric acid solutions become larger than the primary cation yield, $f(H_2O)G(H_2O^+)$, as nitric acid concentration increases. This indicates that the direct action of radiation on nitrate anion and nitric acid contributes to the production of NO_3. It has been shown that the fast formation processes are the same both in nitric acid and nitrate solutions. These results can be explained on the basis of the direct action mechanism for the fast formation process, whereas they are difficult to understand on the basis of the dry hole trapping mechanism. Moreover, according to the dry hole trapping mechanism, we obtained $\sigma_1/\sigma_2 \simeq 4.5$. This means that reaction 10 is 4–5 times more probable than reaction 11. Since reactions 10 and 11 are so fast, H_2O^+ may only react with the adjacent molecules without diffusion. Thus, the reaction probability σ is most probably determined by the probability of finding the specific species surrounding the dry hole (H_2O^+). The high selectivity for nitrate anion is thus less probable. The fast formation process is most probable by the direct dissociation reaction (13).

$$NO_3^- \rightsquigarrow NO_3 + e^- \quad (13)$$

In 6 M nitric acid solutions, 20% of the nitric acid exists in undissociated form.[22] The yield of the fast formation process, however, is in agreement with that in 6 M nitrate solution. This indicates that the direct action on molecular nitric acid is probably reaction 14, but not reaction 15, as proposed earlier.[7]

$$HNO_3 \rightsquigarrow HNO_3^+ + e^- \rightarrow NO_3 + H^+ + e^- \quad (14)$$

$$HNO_3 \rightsquigarrow OH + NO_2 \quad (15)$$

In spite of many studies on the radiolysis of highly concentrated solutions, the nature of direct action and dry hole trapping is still under debate.[3,5,6,30-33] Our results also do not exclude the dry hole trapping mechanism, provided it is not the dominant process. More work is needed to get a better understanding of these processes.

Decay and Reactivity of NO_3. The decay kinetics of NO_3 in the pulse radiolysis of nitric acid solutions has been studied by several authors.[4-8] It has been reported that NO_3 decays by first-order, second-order, or mixed first- and second-order kinetics via reactions 16 and 17. The decay rate has been found to be around 10^4 s^{-1}.[4-8]

$$NO_3 \rightarrow NO_2 + O \quad (16)$$

$$NO_3 + NO_3 \rightarrow N_2O_6 \quad (17)$$

However, in photolysis of ceric nitrate/nitric acid solutions, the decay rate of NO_3 has been found to be around 10^2–10^3 s^{-1}.[15,23,34] In photolysis studies, the reported $2k_{17}/\epsilon$ value is 6.3×10^3 cm s^{-1} [23] ($k_{17} = 4 \times 10^6$ M^{-1} s^{-1} based on $\epsilon = 1300$ M^{-1} cm^{-1}), and the estimated upper limit value of $2k_{17}$ is 6×10^7 M^{-1} s^{-1},[15] whereas much higher $2k_{17}/\epsilon$ values of 1–4×10^6 cm s^{-1} [5] and 2.6×10^6 cm s^{-1} [6,7] have been reported in pulse radiolysis studies. It seems that reaction with radiolytically generated NO_2 radical (reaction 18) is the dominant decay mechanism for NO_3 in pulse radiolysis,[8,15] which has been mistaken for reaction 17 in the early pulse radiolysis studies.

$$NO_2 + NO_3 \rightarrow N_2O_5 \quad (18)$$

In this study, the decay and reactions of NO_3 were examined in 6 M nitric acid solution. The absorbance was monitored at 633 nm with a He–Ne laser as the light source. In 6 M nitric acid solution, OH radical is converted to NO_3 radical via reaction 5. Hydrated electrons and H atoms react quickly via reactions 19–21 with lifetimes much shorter than 1 μs.[20] The products are

$$e_{aq}^- + H^+ \rightarrow H \quad (19)$$

$$e_{aq}^- + NO_3^- \rightarrow NO_3^{2-} \xrightarrow{H_2O} 2OH^- + NO_2 \quad (20)$$

$$H + NO_3^- \rightarrow HNO_3^- \rightarrow OH^- + NO_2 \quad (21)$$

$$NO_3^{2-} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} HNO_3^- \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} H_2NO_3 \ (\rightarrow H_2O + NO_2) \quad (22)$$

in protonation equilibrium (22), with H_2NO_3 being the dominant species in strong acid solution and finally NO_2 is formed.[21]

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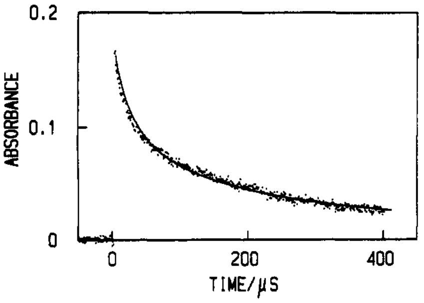

Figure 6. Decay behavior of NO_3 radical in 6 M HNO_3 solution: (dots) experimental data; (—) simulation.

Grätzel et al.[21] reported the half-lives of NO_3^{2-} and HNO_3^- are 12.5 and 3 μs, respectively. No data is available for H_2NO_3. Since protonation accelerates the decay of NO_3^{2-}, we suppose that H_2NO_3 has a half-life comparable to that of HNO_3^-. So, only NO_2 and NO_3 exist as "long-life" intermediates. And the yields of NO_2 and NO_3 are expected to be approximately equal because they represent the reduction and oxidation species. By this assumption, the decay kinetics of NO_3 was simulated, based on the following reactions:[23,35]

$$NO_3 + NO_3 \rightarrow N_2O_6 \quad (4 \times 10^6\ M^{-1}\ s^{-1\ 23}) \tag{17}$$

$$NO_2 + NO_3 \rightarrow N_2O_5 \tag{18}$$

$$NO_2 + NO_2 \rightarrow N_2O_4 \quad (4.5 \times 10^8\ M^{-1}\ s^{-1\ 35}) \tag{23}$$

$$N_2O_4 \rightleftarrows NO_2 + NO_2 \quad (1.5 \times 10^{-5}\ M^{35}) \tag{24}$$

$$N_2O_4 + H_2O \rightarrow HNO_2 + HNO_3 \quad (1 \times 10^3\ s^{-1\ 35}) \tag{25}$$

$$NO_3 + HNO_2 \rightarrow HNO_3 + NO_2 \quad (8 \times 10^6\ M^{-1}\ s^{-1}\ \text{this work}) \tag{26}$$

The value of k_{18} was adjusted to give the best fitting of the experimental results. All other rate constants are reported values (k_{26} evaluated and k_{17} recalculated in this study). As shown in Figure 6, the agreement between the calculation and the experimental data is good. Thus k_{18} was evaluated as $(1.7 \pm 0.3) \times 10^9\ M^{-1}\ s^{-1}$. It should be noted that reactions 17, 25, and 26, which do not contribute appreciably to the decay of NO_3, may be important in steady-state radiolysis. Though less studied in the liquid phase, reaction 18 has been well studied in the gas phase.[36-39] A limiting high-pressure rate constant of $(2.2 \pm 0.5) \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$ has been reported.[37] After conversion of the units, $k_{18} = (1.3 \pm 0.3) \times 10^9\ M^{-1}\ s^{-1}$ in the gas phase, which is comparable with our evaluation in the liquid phase.

For consideration of the reactions of NO_3 with added compounds (reaction 27), a simulation was also carried out in the presence of Ce^{3+} (2, 10 mM), HNO_2 (0.23, 1.25 mM), H_2O_2 (10–40 mM), Ni^{2+} (10 mM), and Co^{2+} (10 mM) based on $k_{18} = 1.7 \pm 0.3 \times 10^9\ M^{-1}\ s^{-1}$. The values of k_{27} were adjusted to

$$NO_3 + S \rightarrow HNO_3 \text{ or } NO_3^- + S' \tag{27}$$

give the best fitting of the experimental results. The calculations agree well with the experimental results. Rate constants of reactions of NO_3 with these compounds were derived as shown in Table II.

TABLE II: Rate Constants for Reactions of NO_3 in 6 M HNO_3 ($M^{-1}\ s^{-1}$)

	k	
reactant	this work	lit.[11]
ethanol	1.2×10^6	$(1.4–3.9) \times 10^6$
2-propanol	2.5×10^6	$(2.4–3.6) \times 10^6$
p-nitroaniline	9.5×10^7	
sulfanilamide	2.4×10^7	
Tl^+	6.8×10^7	$(3.5–8.6) \times 10^7$
Ag^+	2.5×10^9	$(1.5–3.1) \times 10^9$
Mn^{2+}	1.0×10^6	$(1.1–1.5) \times 10^6$
Ni^{2+}	$<4 \times 10^4$	
Cr^{3+}	$<3.5 \times 10^6$	
Co^{2+}	$<1 \times 10^5$	$<7 \times 10^4$
Ce^{3+}	1.4×10^6	$(1.3–1.7) \times 10^6$
H_2O_2	1.9×10^6	
HNO_2	8.0×10^6	
NO_2^- (in 6 M $NaNO_3$)	4.4×10^9	1.2×10^9
SCN^- (in 0.6 M HNO3)	2×10^9	
NO_2	1.7×10^9	1.3×10^9 (gas phase)[37]

In 6 M $NaNO_3$, the decay rate of NO_3 is about 10 times faster. The decay curves of fresh samples could not be fitted by either first-order or second-order decay kinetics. The estimated decay rate is $2 \times 10^5\ s^{-1}$, which is much higher than that reported by Daniels.[5] After two or three electron pulses (1 krad/pulse), the decay curve could be fitted by first-order decay kinetics. The decay rate increases with increasing number of electron pulses. This indicates reactions with radiolytic products are significant. The reaction of NO_3 with NO_2^- (one of the main radiolytic products), was studied in 6 M $NaNO_3$ and the rate constant was evaluated as shown in Table II. The higher decay rate observed in this study is probably because of $NaNO_2$ contained in $NaNO_3$.

Other rate constants shown in Table II were obtained by fitting the decay curves according to first-order decay kinetics. KSCN is not stable in 6 M nitric acid solution.[25] Experiments were carried out in 0.6 M nitric acid solution with addition of 0.1 mM KSCN. Because SCN^- also reacts with OH and NO_3 to yield $(SCN)_2^-$, the absorbance at 640 nm was corrected for contributions from $(SCN)_2^-$. For comparison, reported rate constants are also listed in Table II when available. Our results are consistent with those published results. Presumably, as postulated in recent studies,[8,12,40] NO_3 reacts with organic compounds, H_2O_2, and HNO_2 by H-abstraction reactions and with metal ions, NO_2^-, and SCN^- by electron-transfer reactions.

In γ radiolysis studies of nitric acid solutions, it is impossible to evaluate the yields of HNO_2 and H_2O_2 at the same time because they react with each other.[41] As a result, *p*-nitroaniline and sulfanilamide have been used to scavenge HNO_2 so as to prevent it from reacting with H_2O_2.[42,43] From the previous results, these two compounds may exert dramatic influence on the radiolysis of nitric acid solutions because they react rapidly with NO_3 radical. Our results will help to understand those previously published results.

Acknowledgment. We thank Mr. T. Ueda and Mr. T. Kobayashi for their contributions to this work.

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