Bull. Chem. Soc. Jpn. Vol. 79, No. 8, 1215–1222 (2006)

# Great Enhancement in the Oxidation Ability of Dilute Nitric Acid in Nanoscale Water-Droplets of Reverse Micelle Systems

**Masashi Hojo,* Tadaharu Ueda, Chihiro Daike, Fumiko Takezaki,**
**Yumi Furuya, Kiyomi Miyamoto, Akio Narutaki, and Ryosuke Kato**

Department of Chemistry, Faculty of Science, Kochi University, 2-5-1 Akebono-cho, Kochi 780-8520

Received December 12, 2005; E-mail: mhojo@cc.kochi-u.ac.jp

In reverse micelle systems, a large enhancement of the oxidation ability of dilute nitric acid was discovered, and its oxidation mechanism was explored. The $Br^-$ ion in the surfactant, CTAB, was oxidized to $Br_2$ (or $Br_3^-$) in the $CHCl_3$/CTAB/$H_2O$ reverse micelle system with $W = 1.0$–$4.0$ by diluted nitric acid (0.25–2.5 mol dm$^{-3}$ in 1.0 vol % $H_2O$ portion) at 15–40 °C where CTAB stands for cetyltrimethylammonium bromide, and the $W$ value is the ratio of $[H_2O]$/[surfactant]. At higher concentrations of nitric acid and temperatures, faster reactions occurred. Otherwise, long reaction times were needed, e.g., 10 h for 1.0 mol dm$^{-3}$ $HNO_3$ at 25 °C. Light or ambient oxygen did not appear to affect the reaction. The ratio of produced $Br_2$ or ($Br_3^-$) to the initial amount of $HNO_3$ indicated the following reaction scheme: $2HNO_3 + 2Br^- \rightarrow Br_2 + NO_2^- + NO_3^- + H_2O$. The nitroyl ion (or nitronium ion), $NO_2^+$, was proposed as the intermediate active species. The addition of $HClO_4$ as a proton source caused the complete reduction of N(V) as follows: $NO_3^- + 6H^+ + 5e^- \rightarrow 1/2N_2 + 3H_2O$. The hydrogen-bonding structure of $H_2O$ in the CTAB or CTAC (cetyltrimethylammonium chloride) micelle system was found to be distorted, compared to that in bulk water, by the $^1$H NMR chemical shift of $H_2O$. The change in $^1$H NMR chemical shift also demonstrated the consumption of protons during the oxidation of $Br^-$, but not of $Cl^-$, by dilute $HNO_3$.

The nitrate ion has high chemical stability, especially at low concentrations. Standard redox potentials indicate that it should serve as an excellent oxidizing agent, but in order to react with suitable reactants to form elemental nitrogen or ammonia, special conditions are required, such as the presence of catalysts and high temperature and pressure.[1] Concentrated nitric acid has strong oxidation ability, although dilute nitric acid in aqueous solution at room temperature exhibits no apparent oxidation trend. Cotton and Wilkinson have described that nitric acid with a concentration of less than 2 mol dm$^{-3}$ has almost no oxidation ability.[2] Mixtures of concentrated nitric acid and sulfuric acid ("mixed acid") are used for nitration of organic compounds, and the nitroyl ion (or nitronium ion) $NO_2^+$ is regarded as the active intermediate.[3] Raman spectra of $NO_2^+$ have been observed in solution[4] as well as in the solid state.[5] Using $^{14}$N NMR, Ross et al.[6] have examined the nitric acid/nitronium ion equilibrium in aqueous sulfuric acid. Dimeric nitric acid, $(HNO_3)_2$ or $(DNO_3)_2$, was detected by FTIR in $HNO_3$ or $DNO_3$:$H_2O$:Ar matrices.[7]

We have been studying the structure of water in nanoscale water-droplets of reverse micelles, stabilized by surfactants in organic solvents.[8] The size of the "water-pool" or "water-droplet" may vary from 1 to ≈100 nm, as a linear function of the $W$ value, where $W = [H_2O]/[\text{surfactant}]$.[9] A decrease in the $W$ value, as well as the addition of metal salts at a constant $W$ value caused drastic configuration changes between the octahedral $[Co(H_2O)_6]^{2+}$ (the pale red color) and the tetrahedral $[CoX_4]^{2-}$ ($X = Cl$, Br: the blue color) in $CHCl_3$/[CTAC or CTAB]/$H_2O$ reverse micelle system.[8] It is well known that the properties of water localized in the interior of reverse micelles differ from those of bulk water, and the difference becomes progressively smaller as the amount of water in the micelle system increases.[10]

Many studies have focused on the properties of water or solvation in reverse micelle systems.[11–14] Some researchers have also explored the possibility of using reverse micelle water droplets as "nanoreactors," because their sizes can be controlled,[15,16] or as hosts for proteins and small molecules.[10] Iwamoto et al.[17] have studied the change in the polarization of water in AOT [sodium bis(2-ethylhexyl) sulfosuccinate] reverse micelle spectrophotometrically.

We have proposed that the properties of bulk water should disappear in the conditions that a huge network of water cannot be constructed, since water may gain the properties of bulk water upon the formation of the huge network molecules. In the following cases,[18] water may lose the normal properties, more or less, of the bulk water: (1) the residual water (≈mmol dm$^{-3}$) in organic solvents; (2) aqueous solutions, or organic solvent–water mixtures, containing highly concentrated salts; (3) nanoscale water droplets in nano-tube or reverse micelle systems (the number of water, $n_w < \approx 10^7$); (4) waters on metal electrodes, ion-exchange resins, proteins, the interface of organic solvents, and glass vessels; (5) the water in supercritical conditions. Such waters may be "reduced" to isolated $H_2O$ molecules (as the "dihydrogen ether," [R](H)–O–(H)[R][19c] with poor solvating ability). Concentrated salt effects on the solvolysis rate on typical $S_N1$ substrates, *t*-butyl and adamantyl halides (RX), were elucidated in relation to the interaction between the $X^-$ ion of (or from) the substrate (in the activated state) and added metal ions in the "dihydrogen ether" solution.[19] Based on the Raman spectra,[19c,d] we have demonstrated the distortion of the bulk water structure and

Published on the web August 7, 2006; doi:10.1246/bcsj.79.1215

the alteration of properties of water into those of a "non-aqueous" solvent with the addition of the organic solvents and concentrated salts ($LiClO_4$ and $Et_4NBr$), as well as with increasing temperature.

In the present paper, we would like to report that dilute nitric acid in a small water droplet of reverse micelle systems has an extraordinarily strong oxidation ability, which is strong enough to oxidize $Br^-$ ions to $Br_2$ (or $Br_3{}^-$). $^1H$ NMR was utilized to observe not only changes in hydrogen-bonding structure of $H_2O$ with various $W$ values but also proton consumption during the oxidation reaction in reverse micelles. While studying the configuration changes between octahedral $[Co(H_2O)_6]^{2+}$ and tetrahedral $[CoBr_4]^{2-}$ forms in the $CHCl_3$/CTAB/$H_2O$ reverse micelle system,[8] we observed that a rather strong yellow-color developed only when (dilute) nitric acid was present in $Br^-$ ion rich conditions; the possibility of formation of yellow-colored cobalt(II) and cobalt(III) complexes was denied by our careful examination of many cobalt complexes. Kimura et al.[20,21] have reported the reactions of nitrous and phosphinic acids with the iodide ion in the presence of molecular oxygen in acidic solutions.

## Experimental

**Reagents.** Commercially obtained surfactants were used as received: cetyltrimethylammonium bromide (CTAB, >95% by titration) and chloride (CTAC, 95% by titration) from Wako; sodium bis(2-ethylhexyl) sulfosuccinate (AOT, >99.0%) from Sigma. The amounts of acidic impurities (e.g., $R_3NH^+$) in CTAB and CTAC were evaluated to be ≈0.03 and ≈0.05 mol %, respectively.[8] Chloroform was obtained from Wako and Aldrich as GR grade and ACS reagent grade, containing 0.3–1.0% ethanol and amylenes as the stabilizer, respectively. The chloroform containing ethanol as the stabilizer was used in the experiments, unless otherwise stated. Acetonitrile and dichloromethane ($CH_2Cl_2$) of GR grade from Wako were used as received. Nitric acid (60 and 70%, GR grade) and perchloric acid (70%, GR grade) from Wako were used as purchased.

GR grade bromine ($Br_2$) from Wako, the tribromide salt ($n$-$Bu_4NBr_3$) from Aldrich, $NaNO_3$ and $NaNO_2$ from Wako, sodium hyponitrite hydrate ($Na_2N_2O_2 \cdot xH_2O$), nitronium ($NO_2BF_4$, >95%) and nitrosyl tetrafluoroborate ($NOBF_4$) from Aldrich were used as purchased. Rosaniline (Fuchsin) [4-((4-aminophenyl)(4-imino-2,5-cyclohexadine-1-ylidene)methyl)-2-methylbenzamine monohydrochloride], *o*-tolidine, and DPD (*N*,*N*-diethyl-*p*-phenylenediamine) were purchased from Wako. The following amylenes and related compounds were purchased: 2-metyl-1-butene (>98%), 2-methyl-2-butene (>95%), 2-pentene (>95%), and 1-hexene (>95%) from TCI; 3,3-dimethyl-1-butene (>95%) and 2,3-dimethyl-2-butene (>95%) from Aldrich. Other commercially obtained salts or reagents of GR and ACS reagent grades were used.

**Procedure and Equipment.** Reverse micelle solutions were prepared by adding 0.10 mL of diluted nitric acid of various concentrations to an organic solvent (e.g., $CHCl_3$, total 10 mL finally) containing a surfactant (e.g., CTAB), which was sonicated in an ultrasonic bath for two minutes to make uniform the reverse micelle. The solutions were kept at constant temperatures (e.g., 25 ± 0.02 °C) in a Yamato constant-temperature water bath (Model BK-15), equipped with a cooling dip (Model BE 200F).

UV–visible absorption spectra were measured using a Hitachi double-beam spectrophotometer (Model U-2000) and a Shimadzu (Model UV-2550) in 0.1, 0.2, and 1.0 cm quartz cuvettes at room temperature. All of the absorbance values were converted and are reported as 1.0 cm path length.

$^1H$ NMR measurements of the water in reverse micelle systems were carried out at 25 ± 0.1 °C with JOEL FT-NMR spectrometer (Model JNM-LA400). $D_2O$ in an inner tube was used as the locking solvent, and the spectra were referenced to the $D_2O$ (HOD) signal ($\delta = 4.65$ ppm). An alternate locking solvent ($CDCl_3$, containing TMS) in the inner tube gave minor differences in chemical shift values. The usage of $CDCl_3$ (containing 0.05% TMS) as the reverse micelle system in a single NMR tube gave a tendency similar to the results of double-tube measurements in the region of concern.

**The Detection of $Br_2$ or the $Br_3{}^-$ Ion.** In acidic solutions, Rosaniline reacts with free bromine ($Br_2$) to form red-colored compounds described as either pentabromorosaniline or tetrabromorosaniline.[22] In the present study, the Rosaniline method was slightly adjusted to be used with the chloroform reverse micelle system: An appropriate amount of acetonitrile was added to the reverse micelle system in order to make a (miscible) single-phase solution for $CHCl_3$ and a $H_2SO_4$ aqueous solution. The appearance of the red color around 570 nm confirmed the formation of $Br_3{}^-$ in the reverse micelle system.

**The Formation Constant and Absorptivity of $Br_3{}^-$ in $CHCl_3$.** The interaction between $Br_2$ and $Br^-$ was determined to have a large formation constant, $K = \text{ca. } 3 \times 10^4$ ($Br_2 + Br^- \rightleftharpoons Br_3{}^-$) in $CHCl_3$ at room temperature. A $Br_3{}^-$ salt, $n$-$Bu_4N^+Br_3{}^-$, as well as the free bromine ($Br_2$) in the presence of various concentrations of the bromide ion ($n$-$Bu_4NBr$) were used to evaluate the formation constant. The absorptivity ($\varepsilon$/mol$^{-1}$ dm$^3$ cm$^{-1}$) at $\lambda_{max}$ (273 nm) of $Br_3{}^-$ was estimated to be $5.1 \times 10^4$. Free $Br_2$ gave an absorption peak at 407 nm ($\log \varepsilon = \text{ca. } 2.3$) in $CHCl_3$, cf., $\lambda_{max} = 417$ nm ($\log \varepsilon = 2.32$) in $CCl_4$.[23] We assumed that all of the $Br_2$ was converted into $Br_3{}^-$ in the CTAB reverse micelle at lower $W$ values (e.g., $[Br^-] = 0.28$ mol dm$^{-3}$ at $W = 2.0$). The amount of $Br_2$ (or $Br_3{}^-$) produced by the oxidation of $Br^-$ from CTAB was estimated by the absorbance of $Br_3{}^-$ at 400 nm ($\varepsilon \approx 600$). In the dichloromethane/CTAB reverse micelle and in acetonitrile solution, absorptivity values at 400 nm were evaluated to be similar to that in the chloroform/CTAB reverse micelle. Gabes and Gerding[24] reported the IR and Raman spectra of $Br_3{}^-$, $I_3{}^-$, $IBr_2{}^-$, etc. in the solid state.

## Results and Discussion

**The Formation of $Br_3{}^-$ in $CHCl_3$/CTAB Reverse Micelle System. Effects of the Addition of Salts, the Temperature, and the $W$ Value on Reaction Rates:** A colorless solution of the reverse micelle at $W = 2.0$ ($[H_2O]/[CTAB]$) containing nitric acid with a relatively low concentration, e.g. 1.0 mol dm$^{-3}$ $HNO_3$ in a 0.1 mL $H_2O$ portion (or 0.010 mol dm$^{-3}$ $HNO_3$ in a whole 10 mL $H_2O/CHCl_3$) turned yellow after ca. 8 h at 25 °C (cf., Fig. 1). Increasing the concentration of $HNO_3$, 2.0 and 3.0 mol dm$^{-3}$, caused an increase in absorbance and an acceleration in the reaction rate. The yellow product was identified to be $Br_2$ (or $Br_3{}^-$) by using the Rosaniline method[22] as mentioned in the Experimental section.

The effects of added salts to the reverse micelle system were examined; the addition of $1.0 \times 10^{-2}$ mol dm$^{-3}$ $LiClO_4$ (or 1.0 mol dm$^{-3}$ in the 1.0 vol % amount of $H_2O$) to the reverse micelle containing 0.9 mol dm$^{-3}$ $HNO_3$ caused the solution color to change immediately to yellow. The higher the $LiClO_4$ concentration, the quicker the yellow color developed. Light

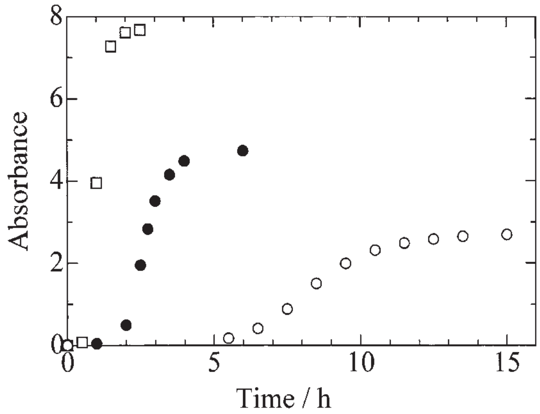

Fig. 1. The change in absorbance at 400 nm with time for various concentrations of $HNO_3$ in the reverse micelle ($CHCl_3$/CTAB) of $W = 2.0$ at 25 °C: (○) 1.0; (●) 2.0; (□) 3.0 mol dm$^{-3}$ $HNO_3$ (in the 1.0 vol % $H_2O$ phase).

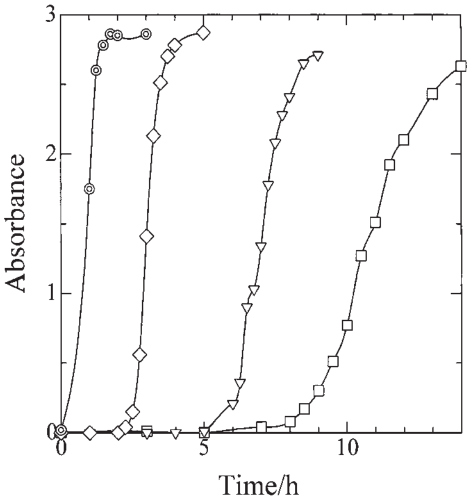

Fig. 2. The change of absorbance at 400 nm with time for 1.0 mol dm$^{-3}$ $HNO_3$ in the reverse micelle ($CHCl_3$/CTAB) of $W = 2.0$ at various temperatures: (□) 25; (▽) 30; (◇) 35; (◎) 40 °C.

over the reaction vessel and ambient oxygen had no apparent effects on the $Br^-$ oxidation; whereas, it has been reported that air, or oxygen gas, affected the oxidation of $I^-$ into $I_3^-$.[20,21] Dilute nitric acid with concentration in the 0.25–2.5 mol dm$^{-3}$ (in 1.0 vol % $H_2O$) range produced almost the half-amount $Br_2$ molecules to each $HNO_3$ molecules. Considering the amount of the product, the formation of $Br_2$ (or $Br_3^-$) seems to follow the reaction in Eq. 1.

$$2HNO_3 + 2Br^- \rightarrow Br_2 + NO_2^- + NO_3^- + H_2O. \quad (1)$$

Other metallic salts, such as $Mg(ClO_4)_2$ and LiBr, also caused the prompt oxidation of $Br^-$ with $HNO_3$ in the reverse micelle at $W = 1.0$ and 2.0. However, no distinct increase in the oxidation rate was observed for non-metal salts, $Me_4NBr$, $Et_4NBr$, $n$-$Bu_4NBr$, and $n$-$Bu_4NClO_4$. Cabos and Delord's neutron scattering data for the (water + NaCl/AOT/heptane) reverse micelle appear to show that water-droplet size is increased by the presence of the electrolyte.[25]

Figure 2 shows the changes in absorbance at 400 nm with time of the CTAB reverse micelle system ($W = 2.0$) in the presence of 1.0 mol dm$^{-3}$ $HNO_3$ at various temperatures. At 25 °C, the formation reaction of $Br_2$ (or $Br_3^-$) did not complete even after 15 h while, at 40 °C, the reaction already completed with a yield greater than 90% (the yield of $Br_2$ with respect to the $HNO_3$ amount) after 2 h. The reaction rate was evaluated at the "half-reaction" time, i.e., the time at which the yield reaches 50% completion for each reaction: ca. 11, 7, 3, and 1 h for 25, 30, 35, and 40 °C for 1.0 mol dm$^{-3}$ $HNO_3$. The "half-reaction" times for various $HNO_3$ concentrations are shown in Fig. 3; the reaction proceeded very quickly at 40 °C for every sample of 1.0–2.5 mol dm$^{-3}$ $HNO_3$ concentration. The yields of $Br_2$ with respect to the amount of $HNO_3$ were ca. 90% at $W = 2.0$.

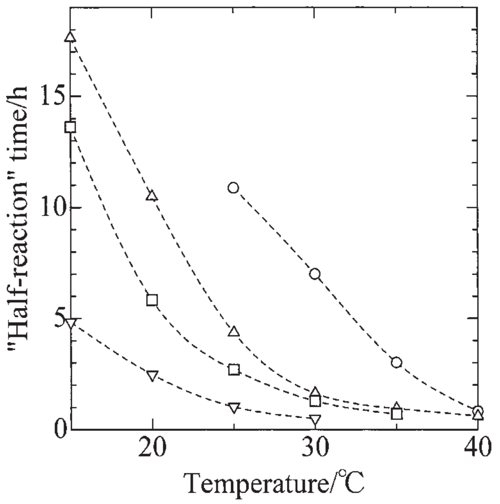

Fig. 3. The effects of temperature on the reaction rates for various $HNO_3$ concentrations at $W = 2.0$: (○) 1.0; (△) 1.6; (□) 2.0; (▽) 2.5 mol dm$^{-3}$ $HNO_3$ (in the $H_2O$ phase).

However, the reaction was slower at lower $W$ values for every $HNO_3$ concentration (1.0–2.5 mol dm$^{-3}$) at a constant temperature. For example, the "half-reaction" time of 4.2, 2.7, and 1.3 h was observed for $W = 1.0$, 2.0, and 4.0, respectively, with 2.0 mol dm$^{-3}$ $HNO_3$ at 25 °C (Fig. 4). Similar decelerations in the reaction rates with decreasing $W$ value were also observed in dichloromethane/CTAB reverse micelle system. It has been noted that the presence of small amounts of water in organic media causes a promotion of the reaction with nitronium salts.[3] At smaller $W$ values, in the present reverse micelle systems, the water-droplets may lose the properties of bulk water to a greater extent, which might cause the decelerated reaction rates.

**The Oxidation of $Br^-$ by $NO_2^+$ and $NO^+$ Ions in Acetonitrile:** The oxidation ability of $NO_2^+$ towards $Br^-$ was examined in acetonitrile solution, becuase the solubility of $NO_2BF_4$ in $CHCl_3$ was too low, cf., Ref. 3. Bontempelli et al.[26] reported electrochemical reduction of $NO_2^+$ and $NO^+$ in acetonitrile. Figure 5 shows that the observed concentrations of $Br_2$ (or $Br_3^-$) from 0.1 mol dm$^{-3}$ $Et_4NBr$ are proportional to the concentrations of $NO_2BF_4$ added; the $Br_2$ concentrations were evaluated to be 1.6, 4.3, and $9.1 \times 10^{-3}$ mol dm$^{-3}$ for 2.0, 5.0, and $10 \times 10^{-3}$ mol dm$^{-3}$ $NO_2BF_4$, using a absorptivity ($\mathcal{E}$) of 600 at 400 nm for $Br_3^-$ in acetonitrile. The stoichiometry between the amounts of $Br_2$ and $NO_2^+$ verified that a two-elec-

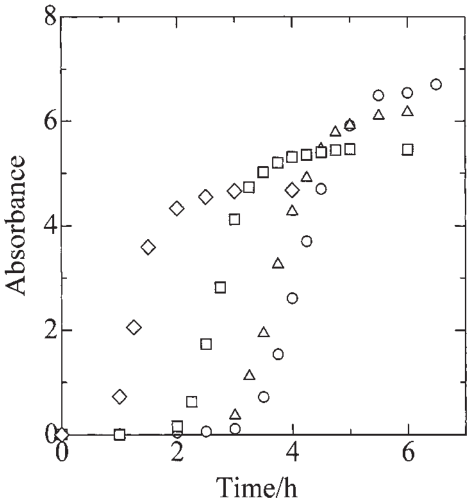

Fig. 4. The change in absorbance at 400 nm with time at various *W* values of the reverse micelle ($CHCl_3$/CTAB) containing 2.0 mol dm$^{-3}$ $HNO_3$ at 25 °C: (○) 1.0; (△) 1.4; (□) 2.0; (◇) 4.0 of the *W* values. The run of *W* = 2.0 in Fig. 4 is different from that in Fig. 1.

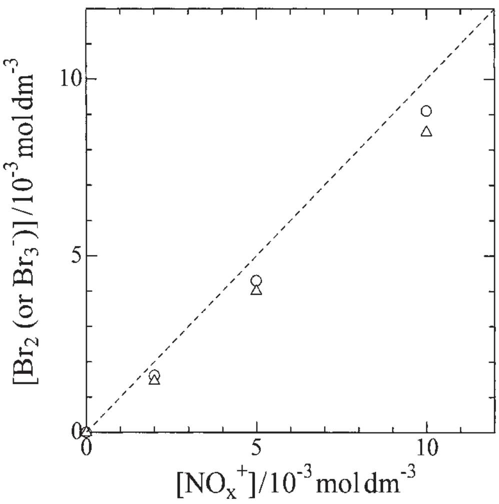

Fig. 5. Observed amounts of $Br_2$ (or $Br_3^-$) from 0.1 mol dm$^{-3}$ $Et_4NBr$ with increasing concentration of $NO_2^+$ and $NO^+$ in acetonitrile: (○) $NO_2BF_4$; (△) $NOBF_4$. The dotted line shows the theoretical value (see the text).

tron oxidation process was occurring, Eq. 2.

$$NO_2^+ + 2Br^- \rightarrow Br_2 + NO_2^-. \tag{2}$$

Similarly, the yield of $Br_2$ from oxidation of $Br^-$ by $NOBF_4$ was 73–85%, and the oxidation process with $NO^+$ can be expressed by Eq. 3.

$$NO^+ + 2Br^- \rightarrow Br_2 + NO^-. \tag{3}$$

In subsequent experiments, dilute nitric acid in acetonitrile was found to oxidize $Br^-$ at 25 °C: nitric acid–MeCN solutions of 0.84–6.7 × $10^{-2}$ mol dm$^{-3}$ in the presence of 0.28 mol dm$^{-3}$ $Et_4NBr$ gave $Br_2$ (or $Br_3^-$) of ca. 70–75% yields after 24 h (Eq. 1). Based on the above experimental results, $NO_2^+$ species is proposed as a reaction intermediate in acetonitrile and also in the reverse micelle.

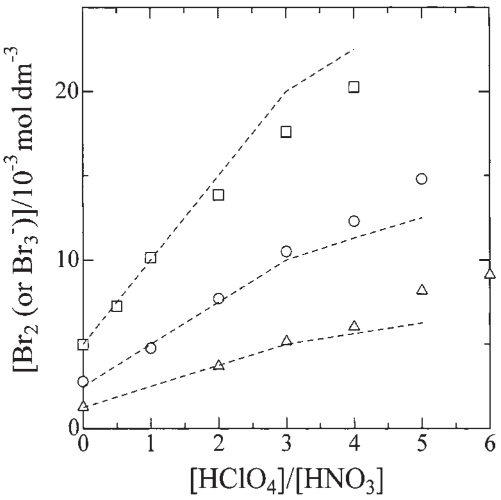

Fig. 6. Observed amounts of $Br_2$ (or $Br_3^-$) from various concentration of $HNO_3$ in the presence of excess amounts of $HClO_4$ in the reverse micelle ($CHCl_3$/CTAB) of *W* = 2.0: (△) 0.25; (○) 0.50; (□) 1.0 mol dm$^{-3}$ $HNO_3$. The dotted lines show the theoretical values (see the text).

**The Oxidation of $Br^-$ with $HNO_x$ ($x$ = 1, 2, and 3) in the Presence of Excess Amounts of Protons. The Addition of $HClO_4$ to $HNO_3$:** As mentioned above, the amount of $Br_2$ produced from the oxidation of $Br^-$ with diluted nitric acid was found to be proportional to the concentration of $HNO_3$ in the water-droplets (of 1.0 vol % $H_2O$) of the reverse micelle system. The addition of $HClO_4$, as the proton source, to the $HNO_3$ system caused a remarkable increase not only in the reaction rate but also in the amount of $Br_2$. For example with $HNO_3$ concentrations of 0.50 mol dm$^{-3}$, the presence of the 2 and 4 equivalents of $H^+$ to a unit of $NO_3^-$ ($[HClO_4]/[HNO_3]$ = 1 and 3 in Fig. 6) gave the 1 and 2 equivalents of $Br_2$, respectively. Similar results were observed for 0.25 and 1.0 mol dm$^{-3}$ $HNO_3$ systems. The following oxidation mechanisms are proposed:

$$NO_3^- + 2H^+ \rightarrow NO_2^+ + H_2O \rightarrow NO_2^- - 2e^-, \tag{4}$$

$$NO_2^- + 2H^+ \rightarrow NO^+ + H_2O \rightarrow NO^- - 2e^-. \tag{5}$$

The oxidation steps expressed by Eqs. 4 and 5 are both two-electron processes. The next step is thought to be Eq. 6. However, the amount of $Br_2$ was more or less than the amount theoretically predicted.

$$NO^- + 2H^+ \rightarrow N^+ + H_2O \rightarrow 1/2N_2 - e^-. \tag{6}$$

Note that the ratio of the number of electrons to the added proton concentration ($1e^-/[2H^+]$) in Eq. 6 is the half, compared with that ($2e^-/[2H^+]$) in Eq. 4 or 5, and the difference resulted in the differet slope in Fig. 6. The overall reaction should be Eq. 7.

$$NO_3^- + 6H^+ + 5e^- \rightarrow 1/2N_2 + 3H_2O. \tag{7}$$

The standard redox potential of Eq. 7 is reported to be very high, i.e., $E^o = 1.246$ V.[27,28] Considering the excess amount of the $Br_2$ production, the final product from $NO_3^-$ can be $NH_3OH^+$ as well as $N_2$.[27,28] The standard potentials of $Br_2$ and $Br_3^-$ in aqueous solution are 1.087 and 1.050 V, respectively.[28]

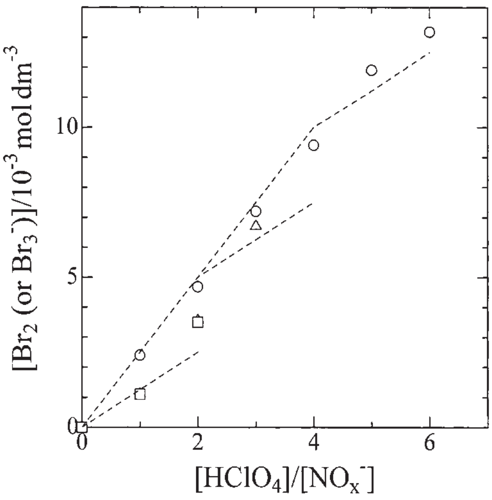

Fig. 7. Observed amounts of $Br_2$ (or $Br_3^-$) from $NO_3^-$, $NO_2^-$, or $NO^-$ with increasing concentration of $HClO_4$ in the reverse micelle ($CHCl_3$/CTAB) of $W = 2.0$: (○) 0.5 mol dm$^{-3}$ $NaNO_3$; (△) 0.50 mol dm$^{-3}$ $NaNO_2$; (□) 0.25 mol dm$^{-3}$ $Na_2N_2O_2$ (in 1.0 vol % $H_2O$ phase). The dotted lines show the theoretical values (see the text).

$$Br_2 + 2e^- \rightleftharpoons 2Br^- \quad (E^\circ = 1.087\,V). \tag{8}$$

$$Br_3^- + 2e^- \rightleftharpoons 3Br^- \quad (E^\circ = 1.050\,V). \tag{9}$$

Oxidation potential of nitric acid is high enough to oxidize $Br^-$ into $Br_2$ or $Br_3^-$ in solution; however, it seems not to be strong enough to oxidize $Cl^-$ to $Cl_2$ ($E^\circ = 1.396$ V).[28]

**The Addition of $HClO_4$ to $NaNO_3$, $NaNO_2$, and $Na_2N_2O_2$:** Ogawa et al.[29] examined the electrochemical reduction of the nitrate ion at mercury electrodes in the presence of metal ions to explore why the nitrate ion (nitric acid) is a powerful oxidizing agent in acidic solution and not an oxidizing agent in neutral or alkaline solution. Figure 7 shows the oxidation abilities of $NO_3^-$, $NO_2^-$, and $NO^-$ ($N_2O_2^{2-}$) in the absence and in the presence of protons using the CTAB reverse micelle at $W = 2.0$. A 0.50 mol dm$^{-3}$ $NaNO_3$ (in the 1.0 vol % $H_2O$ phase) reversed micelle without $H^+$ did not oxidize $Br^-$; however, in the presence of $HClO_4$, the $NO_3^-$ ion oxidized $Br^-$ to $Br_2$ (or $Br_3^-$). The amounts of $Br_2$ for $[HClO_4]/[NO_3^-] = 0$–6 seemed to be accordance with the reaction mechanism in Eqs. 4–6. The oxidation of $Br^-$ did not occur in solutions containing either 0.5 mol dm$^{-3}$ $NaNO_2$ or 0.25 mol dm$^{-3}$ $Na_2N_2O_2$ without the addition of protons. Although, in the presence of $HClO_4$, the oxidation of $Br^-$ into $Br_2$ occurred quite well, it was rather difficult to fit precisely the experimental and theoretical values to each other. At any rate, these results suggested the reduction of N atom from a +5 oxidation state to a 0 oxidation state. The overall reaction scheme should follow the scheme in Eq. 7.

The quantitative formation of $Br_3^-$ was observed in the $CH_2Cl_2$ reverse micelle, as well as the $CHCl_3$ reverse micelle system. The reverse micelle system with an anionic surfactant, AOT ($W = 2.0$–10.0), and heptane as the solvent, also, oxidized $Br^-$ to $Br_3^-$ in the presence of 0.1 mol dm$^{-3}$ $n$-$Bu_4NBr$. In the $CHCl_3$/CTAC reverse micelle system, however, no oxidation of $Cl^-$ to $Cl_2$ was detected using *o*-tolidine[30] and DPD (*N*,*N*-diethyl-*p*-phenylenediamine),[31] as indicators; while the formation of $Br_2$ was detected in the $CHCl_3$ reverse micelle system. The fact that $Cl^-$ was not oxidized by dilute $HNO_3$ was confirmed also by $^1$H NMR chemical shift of $H_2O$ in the $CHCl_3$/CTAC reverse micelle system (vide infra). The oxidation of $Cl^-$ to $Cl_2$ by the nitrate radical, $NO_3^\bullet$, in aqueous solution has been reported, though.[32]

**Effects of Alcohols and Amylenes in $CHCl_3$:** Commercially obtained chloroform usually contains small amounts of stabilizers, such as ethanol or amylenes, and the effects of these compounds on the oxidation $Br^-$ were examined in the $CHCl_3$/CTAB reverse micelle at $W = 2.0$ containing 2.0 mol dm$^{-3}$ $HNO_3$ at 25 °C. The addition of 1.0, 2.0, and 5.0 vol % ethanol to the reverse micelle system caused observable decreases in the reaction rate: ca. 1, 2, and 6 h delay, respectively, compared with the system of original chloroform containing 0.3–1.0% EtOH. The effects of 1.0, 2.0, and 5.0 vol % octanol were slightly smaller than those of ethanol. However, the addition of acetonitrile slightly accelerated the oxidation reaction rates. Acetonitrile, present not only in the organic phase but also in the water-droplets, may distort the water structure further, whereas, octanol may encapsulate water-droplets and stabilize the water structure through the OH of the alcohol. The addition of alcohols and acetonitrile did not influence the final yield of $Br_2$ (or $Br_3^-$).

In the course of the present study, however, we noticed that the yield of $Br_2$ (or $Br_3^-$) produced using the CTAB reversed micelle system were too small, especially with lower concentrations of $HNO_3$, whenever chloroform containing amylenes was used as the solvent. Amylenes include several alkenes, i.e., 1-pentene, 2-pentene, 2-methyl-1-butene, and 2-methyl-2-butene, and the effects of amylene and related compounds on the production of $Br_2$ (or $Br_3^-$) were examined. Figure 8 shows the amount of $Br_3^-$ produced using the CTAB reverse micelle system containing 2.0 mol dm$^{-3}$ $HNO_3$ in the presence of various amounts of 2-methyl-2-butene at 35 °C. Without the alkene, more than 95% yield of $Br_2$ was obtained; however,

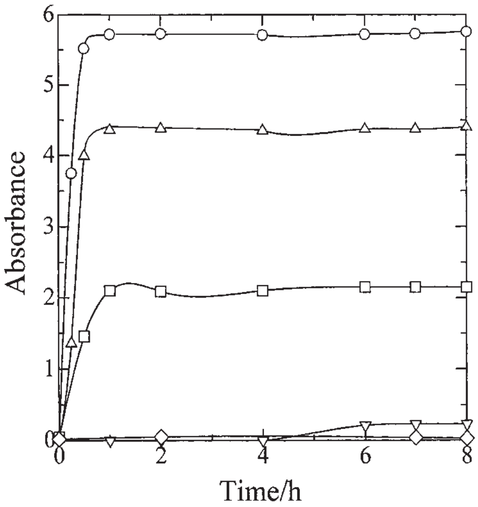

Fig. 8. The change in absorbance at 400 nm with time for 2.0 mol dm$^{-3}$ $HNO_3$ (in a 1.0 vol % $H_2O$ phase) in the presence of various concentrations of 2-methyl-2-butene in the reverse micelle ($CHCl_3$/CTAB) of $W = 2.0$ at 35 °C: (○) 0; (△) 0.002; (□) 0.005; (▽) 0.0075; (◇) 0.01 mol dm$^{-3}$ 2-methyl-2-butene.

Table 1. The Yields of $Br_2$ (or $Br_3^-$) from 2.0 mol dm$^{-3}$ $HNO_3$[a)] (or 0.020 mol dm$^{-3}$ $HNO_3$ as the Whole Solution) in the Presence of Various Concentrations of Alkene Compounds in $CHCl_3$/CTAB of $W = 1.4$ at 25 °C

| Concn of alkenes /mol dm$^{-3}$ | 0 | 0.002 | 0.005 | 0.0075 | 0.01 |
|---|---|---|---|---|---|
| 3,3-Dimethyl-1-butene | 100% | 89% | 50% | 16% | 1% |
| 2,3-Dimethyl-2-butene | 99% | 72% | 0% | 0% | 0% |
| 2-Methyl-1-butene | 98% | 77% | 39% | 5% | 1% |
| 2-Methyl-2-butene | 97% | 69% | 37% | 11% | 0% |
| 1-Hexene | 100% | 73% | 40% | 8% | 1% |
| 2-Pentene | 100% | 75% | 37% | 7% | 1% |
| Theoretical value[b)] | 100% | 80% | 50% | 25% | 0% |

a) In the water-droplets (1.0 vol %) in the micelle system. b) Nitric acid of 0.02 mol dm$^{-3}$ can form 0.01 mol dm$^{-3}$ $Br_2$, which reacts an alkene to form the dibromoalkane.

addition of 2-methyl-2-butene caused decreases in the yield: ca. 75, 40, 10, and 0% yield with 0.002, 0.005, 0.0075, and 0.01 mol dm$^{-3}$ 2-methyl-2-butene, respectively. The above results indicate that $Br_2$, produced in the oxidation reaction, reacts with the butene stoichiometrically to form, probably, the dibromobutane through common reaction pathways.[33]

Another alkene, 1-hexene, caused a distinct decrease in the reaction rate and in the final yield of $Br_2$ using similar experimental conditions at 25 °C. However, this system gave an interesting time change in the $Br_2$ concentration for the cases especially with 0.0075 or 0.01 mol dm$^{-3}$ of 1-hexene. With 0.01 mol dm$^{-3}$ of 1-hexene, for instance, the production of a small amount of $Br_3^-$ was observed after 3.5 h but it decreased gradually to disappear completely after 6 h. The tentative formation of the $Br_3^-$ species was confirmed by the appearance and the disappearance of the absorption peak at around 273 nm as well as tailing at 400 nm. A similar but more distinct change in $Br_3^-$ production was observed with 0.01 mol dm$^{-3}$ 3-methyl-1-butene or 3,3-dimethyl-1-butene. On the other hand, 2-methyl-2-butene (as described above) and 2-pentene did not alter the reaction behavior. The different behavior between 1-alkenes and 2-alkenes can be attributed to the reaction rates of $Br_2$ toward the alkenes; the bromination of 2-alkenes is much faster than that of 1-alkenes because 2-alkenes have more electron-donating groups than 1-alkenes.[34] Table 1 shows the final yields of $Br_3^-$ in the reverse micelle of $W = 1.4$ at 25 °C. Interestingly, when 0.005–0.01 mol dm$^{-3}$ of 2,3-dimethyl-2-butene was added, no $Br_3^-$ was produced; the intermediate species $NO_2^+$ may have attacked directly the butene due to its greater electron density. The nitration of phenol compounds by dilute nitric acid in reverse micelle systems will be reported later.

**Observation by $^1$H NMR of the Water Structure Changes in Reverse Micelle Systems.** The states of the water in AOT reverse micelles in heptane were investigated by $^1$H and $^{23}$Na NMR spectroscopy[11] over a large $W$ value range ($1.6 < W < 50$): in the $^1$H NMR spectrum, the chemical shift of $H_2O$ shifted downfield with an increase in the amount of water and gradually approached that of ordinary water.

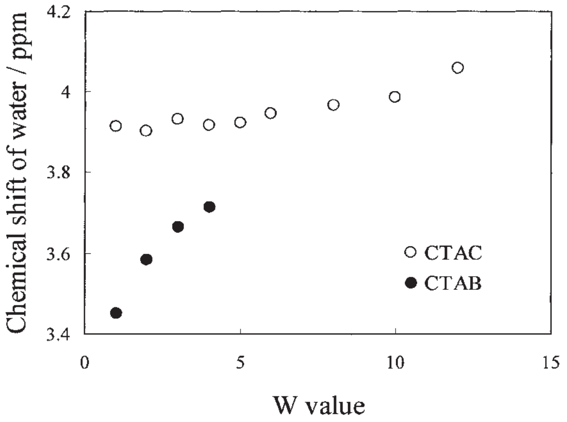

Fig. 9. Changes in the $^1$H NMR chemical shift value of water with the $W$ value in the reverse micelle, $CHCl_3$/CTAB or CTAC/$H_2O$ (of 1.0 vol %) at 25 °C: (●) CTAB; (○) CTAC.

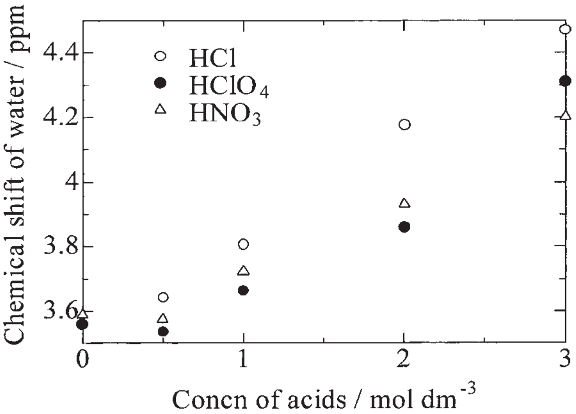

Fig. 10. Changes in the $^1$H NMR chemical shift value of water in the reverse micelle, $CHCl_3$/CTAB/$H_2O$ (of 1.0 vol %) versus increasing concentrations of strong acids at 25 °C: (○) HCl; (△) $HNO_3$, measured just after preparation; (●) $HClO_4$.

Figure 9 shows the change in the chemical shift of $H_2O$ in $CHCl_3$/CTAB and CTAC reverse micelle systems with various $W$ values at 25 °C. The chemical shift ($\delta$) decreased remarkably with decreasing $W$ value for CTAB ($W = 1.0$–$4.0$). The decrease in the chemical shift value of $H_2O$ indicates that the hydrogen-bonding structure of water has been distorted. However, the CTAC system showed smaller gradual decrease in $\delta$ value than the CTAB system. The difference between CTAB and CTAC may be caused by the water-distortion ability of ions due to sizes of $Br^-$ and $Cl^-$. At any rate, the $\delta$ values of water in the reverse micelle systems are much smaller than that of bulk water ($\delta \approx 4.7$),[18,35] which indicates the hydrogen-bonding structure of water in the reverse micelle systems is indeed distorted, compared with that of bulk water. Higuchi and Misra[36] demonstrated that the activity of water in AOT-hydrocarbon reverse micelles decreased as the $W$ value decreased. For the alternate changes in the O–H stretching region of $H_2O$/AOT/heptane with $W$ values, D'Aprano et al.[37] assigned "bonded" and "bulk" waters.

Figure 10 shows the effects of strong acids, such as HCl, $HNO_3$, and $HClO_4$, on the $\delta$ value of $H_2O$ in the $CHCl_3$/CTAB reverse system of $W = 2.0$ at 25 °C. The sample of $HNO_3$ was used just after preparation because the oxidation

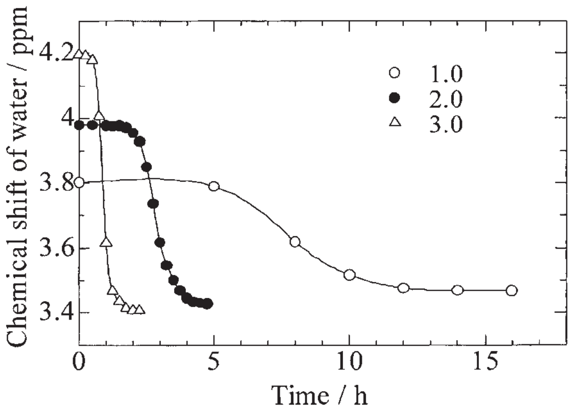

Fig. 11. Changes in the $^1$H NMR chemical shift value of water with time in the reverse micelle, $CHCl_3$/CTAB/$H_2O$ (1.0 vol %), at $W = 2.0$ versus $HNO_3$ concentration at 25 °C: (○) 1.0; (●) 2.0; (△) 3.0 mol dm$^{-3}$ $HNO_3$ (in the 1.0 vol % $H_2O$ phase).

reaction proceeded as a function of time. In increasing the concentration of the strong acids caused an increase in the $\delta$ value. Hydrochloric acid gave the largest effect among all the acids while perchloric acid gave the least effect, up to 2 mol dm$^{-3}$ salt concentrations. These results are probably based on the difference of anion effects; we have observed that anions with the larger crystal ionic radius cause the larger effects on the chemical shifts of water towards upper-field, as $Cl^- < NO_3^- < Br^- < I^- \approx ClO_4^-$, in 2.0%[38] and 20 vol % EtOH–$H_2O$ solutions.[39] The $^1$H NMR chemical shift can identify the presence of strong acids in reverse micelle systems, as well as in bulk water or bulk $H_2O$–EtOH mixed solution.

Figure 11 shows the change in $\delta$ value with time of $H_2O$ in the $CHCl_3$/CTAB reverse micelle system of $W = 2.0$ containing 1.0, 2.0, and 3.0 mol dm$^{-3}$ $HNO_3$ (in the 1.0 vol % water) at 25 °C; all of the solutions became yellow in NMR tubes, indicating the formation of $Br_3^-$. The $\delta$ values decreased with time in accordance with the formation of $Br_3^-$ (cf. Fig. 1) and the decreases in $\delta$ values correspond to the decreases in the $HNO_3$ concentrations in the CTAB reverse micelle systems. Now, the consumption of protons during the oxidation reaction (Eq. 1) was verified. The decrease in the $\delta$ value was observed for CTAB reverse micelle of $W = 4.0$ as well as 2.0 at 25 °C. As for the $CHCl_3$/CTAC system of $W = 4.0$, however, the original $\delta$ value (2 mol dm$^{-3}$ $HNO_3$) of ca. 4.22 ppm remained constant even after six days, meaning that $Cl^-$ is not oxidized by $HNO_3$.

## References

1 J. C. Fanning, *Coord. Chem. Rev.* **2000**, *119*, 159.

2 F. A. Cotton, G. W. Wilkinson, *Advanced Inorganic Chemistry: A Comprehensive Text*, 4th ed., John Wiley & Sons, New York, **1980**, Chap. 13.

3 G. A. Olah, R. Malhotra, S. C. Narang, *Nitration: Methods and Mechanisms*, VCH, New York, **1989**.

4 N. C. Marziano, P. G. Traverso, A. D. Santis, M. Sampoli, *J. Chem. Soc., Chem. Commun.* **1978**, 873.

5 J. W. Nebgen, A. D. McElroy, H. F. Klodowski, *Inorg. Chem.* **1965**, *4*, 1796.

6 D. S. Ross, K. F. Kuhlmann, R. Malhotra, *J. Am. Chem. Soc.* **1983**, *105*, 4299.

7 P. R. McCurdy, W. P. Hess, S. S. Xantheas, *J. Phys. Chem. A* **2002**, *106*, 7628.

8 H. Nagayama, M. Hojo, T. Ueda, Y. Nishimori, M. Okamura, C. Daike, *Anal. Sci.* **2001**, *17*, 1413.

9 *Structure and Reactivity in Reverse Micelles*, ed. by M. P. Pileni, Elsevier, Amsterdam, **1989**.

10 P. L. Luisi, M. Giomini, M. P. Pileni, B. H. Robinson, *Biochim. Biophys. Acta* **1988**, *947*, 209.

11 M. Wong, J. K. Thomas, T. Nowak, *J. Am. Chem. Soc.* **1977**, *99*, 4730.

12 L. Garcia-Rio, J. R. Leis, J. C. Mejuto, M. E. Pena, *Langmuir* **1994**, *10*, 1676.

13 K. K. Karukstis, A. A. Frazier, D. S. Martula, J. A. Whiles, *J. Phys. Chem.* **1996**, *100*, 11133.

14 H. Shirota, K. Horie, *J. Phys. Chem. B* **1999**, *103*, 1437.

15 J. H. Fendler, *Chem. Rev.* **1987**, *87*, 877.

16 I. B. Blagoeva, P. Gray, M.-F. Ruasse, *J. Phys. Chem.* **1996**, *100*, 12638.

17 J. Nishimoto, E. Iwamoto, T. Fujiwara, T. Kumamaru, *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 535.

18 M. Hojo, *Bunseki Kagaku* **2004**, *53*, 1279; M. Hojo, *Kharkov Univ. Bull.* **2004**, *626*, Chemical Series 11(34), 47.

19 a) L. C. Manege, T. Ueda, M. Hojo, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 589. b) L. C. Manege, T. Ueda, M. Hojo, M. Fujio, *J. Chem. Soc., Perkin Trans. 2* **1998**, 1961. c) M. Hojo, T. Ueda, S. Inoue, Y. Kawahara, *J. Chem. Soc., Perkin Trans. 2* **2000**, 1735. d) M. Hojo, T. Ueda, E. Ueno, T. Hamasaki, D. Fujimura, *Bull. Chem. Soc. Jpn.*, in press.

20 M. Kimura, M. Sato, T. Murase, K. Tsukahara, *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2900.

21 M. Kimura, N. Ieyama, M. Matsumoto, K. Shimada, K. Tsukahara, *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1871.

22 E. R. Wright, R. A. Smith, B. G. Messick, In *Colorimetric Determination of Nonmetals*, ed. by D. F. Bolltz, J. A. Howell, John Wiley & Sons, New York, **1978**, Chap. 2, p. 47.

23 *Kagaku Binran, Kiso-Hen*, 5th ed., Chemical Society of Japan, Maruzen, Tokyo, **2004**, p. II-748.

24 W. Gabes, H. Gerding, *J. Mol. Struct.* **1972**, *14*, 267.

25 C. Cabos, P. Delord, *J. Phys. Lett.* **1980**, *41*, L-455.

26 G. Bontempelli, G.-A. Mozzocchin, F. Magno, *J. Electroanal. Chem.* **1974**, *55*, 91.

27 *Encyclopedia of Electrochemistry of the Elements*, ed. by A. J. Bard, Mercel Dekker, New York, **1978**, Vol. 8, Chap. VIII-5.

28 *Standard Potentials in Aqueous Solution*, ed. by A. J. Bard, R. Parsons, J. Jordan, Mercel Dekker, New York, **1985**.

29 N. Ogawa, R. Kikuchi, A. Nakamura, H. Aizawa, S. Ikeda, *Anal. Sci.* **1993**, *9*, 847; N. Ogawa, H. Kodaiku, S. Ikeda, *J. Electroanal. Chem.* **1986**, *208*, 117; N. Ogawa, K. Yokoi, I. Watanabe, S. Ikeda, *Denki Kagaku* **1992**, *60*, 26.

30 E. R. Wright, R. A. Smith, B. G. Messick, In *Colorimetric Determination of Nonmetals*, ed. by D. F. Bolltz, J. A. Howell, John Wiley & Sons, New York, **1978**, Chap. 4, p. 88; J. D. Johnson, R. Overby, *Anal. Chem.* **1969**, *41*, 1744.

31 *Standard Methods for the Examination of Water and Wastewater*, 17th ed., ed. by L. S. Clesceri, A. E. Greenberg, R. R. Trussell, American Public Health Association, Washington, **1989**, pp. 4–62.

32 G. A. Poskrebyshev, R. E. Huie, P. Neta, *J. Phys. Chem. A* **2003**, *107*, 1964.

33 R. T. Morrison, R. N. Boyd, *Organic Chemistry*, 6th ed., Prentice-Hall, New York, **1992**, Chap. 9.

34 P. Sykes, *A Primer to Mechanism in Organic Chemistry*, Longman, London, **1995**, Chap. 5.

35 R. M. Silverstein, G. C. Bassler, T. C. Morrill, *Spectrometric Identification of Organic Compounds*, 5th ed., John Wiley & Sons, New York, **1991**, Chap. 5; F. X. Webster, J. R. West, R. M. Silverstein, *Aldrichimica Acta* **1985**, *18*, 58; **1985**, *18*, 70.

36 W. I. Higuchi, J. Misra, *J. Pharm. Sci.* **1962**, *51*, 455.

37 A. D'Aprano, A. Lizzio, U. T. Liveri, F. Aliotla, C. Vasi, P. Migliardo, *J. Phys. Chem.* **1988**, *92*, 4436.

38 M. Hojo, R. Kato, unpublished data.

39 A. Nose, M. Hojo, T. Ueda, *J. Phys. Chem. B* **2004**, *108*, 798.