

# Oxidative dissolution of $\text{Tc(IV)O}_2 \cdot n\text{H}_2\text{O}$ colloids by sonolysis

By T. Sekine<sup>1,2,\*</sup> and M. Zakir<sup>2</sup>

<sup>1</sup> Center for the Advancement of Higher Education, Tohoku University, 980-8576 Sendai, Japan

<sup>2</sup> Department of Chemistry, Graduate School of Science, Tohoku University, 980-8578 Sendai, Japan

(Received August 24, 2007; accepted in revised form February 25, 2008)

*Tc(IV) oxide colloids / Sonolysis / Cavitation / H, OH radicals*

**Summary.** Redox reactions of Tc in aqueous solutions by sonolysis were investigated. Aqueous pertechnetate ( $\text{Tc(VII)O}_4^-$ ) solutions and  $\text{Tc(IV)O}_2 \cdot n\text{H}_2\text{O}$  colloids solutions were sonicated (200 kHz, 200 W) in a glass cell with flat bottom under Ar or He atmosphere at 20 °C. No reduction of  $\text{TcO}_4^-$  was observed in this study. However, we found that the  $\text{TcO}_2 \cdot n\text{H}_2\text{O}$  colloids dispersed in an aqueous solution were completely dissolved by ultrasonic irradiation within 30 min under Ar atmosphere, and  $\text{TcO}_4^-$  was eventually produced. The production of  $\text{TcO}_4^-$  was considerably suppressed in the presence of *t*-butyl alcohol (an effective scavenger of OH radicals), indicating that Tc(IV) was oxidized by OH radicals (produced by dissociation of water molecules) in hot cavitation bubbles created by ultrasound. The formation rate of  $\text{TcO}_4^-$  under He atmosphere was smaller than that under Ar atmosphere. This can be attributed to a difference of the effective maximum temperature in the collapsing bubbles. Because thermal conductivity of He is much higher than Ar, thermal transport effectively occurs from the bubbles to the surrounding liquid. Thus, temperature of cavitation bubbles filled with He should be lower than those filled with Ar, resulting in the smaller OH formation rate.

## Introduction

Technetium-99 is a long-lived fission product with a half-life of  $2.11 \times 10^5$  y. It is produced in appreciable amounts (thermal neutron fission yield = 6.1%) in nuclear fuel. Because of its long half-life, the migration of <sup>99</sup>Tc in the environment is of great importance from a viewpoint of high-level radioactive wastes disposal in deep underground. The mobility of technetium in aqueous medium depends on its redox conditions. It exists as pertechnetate ( $\text{Tc(VII)O}_4^-$ ), which is well known as a highly soluble and mobile species, in oxidizing conditions, whereas Tc(IV) ( $\text{TcO(OH)}_2$ ,  $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ ) is formed as insoluble and immobile species under reducing atmosphere such as deep underground.

Recently, radiolytic reactions of technetium have been extensively investigated [1–10]. Because a high dose is anticipated to surroundings from the wastes for a long period

of time, it is important to know radiolytic effects on alteration of a matrix of waste materials itself and a change of chemical species of radionuclides. Said *et al.* [1] found a brown turbid solution by irradiation of aqueous  $\text{TcO}_4^-$  solutions in carbonate media with <sup>60</sup>Co  $\gamma$ -rays, and they concluded the formation of Tc(IV) colloids. Lukens *et al.* [2] reported that  $\text{TcO}_4^-$  was efficiently reduced during radiolysis in the excess nitrate solution, and they analyzed the structure of  $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ , as radiolytic products in alkaline solutions, by EXAFS [3]. We have reported the formation of nanoparticles of  $\text{TcO}_2 \cdot n\text{H}_2\text{O}$  by Bremsstrahlung irradiation of aqueous  $\text{TcO}_4^-$  solutions [4] and clarified the reduction mechanisms initiated by hydrated electrons in neutral solutions. A soluble Tc(IV) species as a precursor of  $\text{TcO}_2 \cdot n\text{H}_2\text{O}$  colloids was radiolytically formed when acidic solutions of  $\text{TcO}_4^-$  were irradiated [5, 6]. The soluble Tc(IV) species was chemically synthesized by Vichot *et al.* and its structural analysis was made by EXAFS [7]. Furthermore, its chemical properties were extensively investigated [8]. Thus, chemical species of technetium produced by radiolysis have been clarified step by step, and it was recognized that radiolytic products of water molecules (hydrated electrons, H, OH radicals and so on) played an important role on the redox reactions of technetium.

Unique radical reactions are also expected by sonolysis. The chemical effects of ultrasound are driven primarily from acoustic cavitation, namely the formation, growth and implosive collapse of tiny bubbles in medium [11]. Bubble collapse in liquids results in an enormous concentration of energy by adiabatic contraction of bubble volume, and it results high temperature (5000 K [12]) and high pressure (300 bar [12]) interior the bubble. In an aqueous media, water molecules in the bubble are partly dissociated, resulting in the formation of H and OH radicals in and around the bubbles. Radical reactions with technetium by sonolysis are of scientific interest compared with radiolytic reactions studied before.

In this paper, we report sonolytic effects on technetium in aqueous solutions focused on the redox reactions of Tc(VII) ( $\text{TcO}_4^-$ ) and Tc(IV) ( $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ ) which are the main final chemical species found in radiolytic reactions in aqueous solutions. We have found that  $\text{TcO}_2 \cdot n\text{H}_2\text{O}$  colloids dispersed in an aqueous solution were easily oxidized by ultrasonic treatment for 30 min under Ar atmosphere, and  $\text{TcO}_4^-$  was eventually formed. The oxidation kinetics is discussed.

\* Author for correspondence  
(E-mail: tsekine@mail.tains.tohoku.ac.jp).

## Experimental

Technetium-99 ( $\text{NH}_4^{99}\text{TcO}_4$  or  $\text{K}^{99}\text{TcO}_4$ ) was purchased from the Radiochemical Center, Amersham. Its crystal was dissolved in triply distilled water and the  $\text{TcO}_4^-$  concentration of the solution was adjusted to  $10^{-4}$  M for sonolysis. Hydrosols of  $\text{TcO}_2 \cdot n\text{H}_2\text{O}$  nanoparticles were prepared by radiolysis of  $\text{TcO}_4^-$  as reported previously [4–6]. The aqueous solutions of  $\text{TcO}_4^-$  were sealed in polypropylene vials (5 mL in volume) after Ar-bubbling, and were irradiated with Bremsstrahlung from an electron linear accelerator of the Laboratory of Nuclear Science, Tohoku University. The electrons (30 MeV) were converted to Bremsstrahlung by hitting a platinum converter (1 mm thick), and were removed with a sweep magnet behind the converter. The temperature of the target solutions was maintained at  $17 \pm 3$  °C during the irradiation with a cooling system [4]. The conversion yields from Tc(VII) to Tc(IV) were larger than 90%. The dispersed solutions were kept in a refrigerator (5 °C). The colloids were centrifuged and washed with triply distilled water prior to use, then dispersed again in aqueous media. The concentration of  $^{99}\text{Tc(IV)}$  was adjusted from 10  $\mu\text{M}$  to 0.1 mM for sonolysis experiments.

In the Bremsstrahlung irradiation of aqueous solutions of  $\text{TcO}_4^-$ , colloid formation is pH dependent [5]. When its pH is lower than 3, soluble Tc(IV) oxide polymer [7] is produced [5], whereas the  $\text{TcO}_2 \cdot n\text{H}_2\text{O}$  colloids are formed at pH higher than 3. In this study, only neutral dispersed solutions of the  $\text{TcO}_2 \cdot n\text{H}_2\text{O}$  colloids were used for sonolysis.

Ultrasonic treatment was carried out using a 65 mm  $\varnothing$  oscillator (Barium titanate) and an ultrasonic generator (Kaijo 4021, frequency 200 kHz) operated at 200 W. A schematic figure of the sonication system is shown in Fig. 1. A cylindrical glass vessel with a flat bottom (inner diameter 25 mm  $\varnothing$ , bottom thickness 1 mm) was used for sonication of the sample solutions. One of the side arms connected to a quartz cell enables spectrophotometric measurements of the solutions without exposure to air. Another has a silicon rubber septum for sampling an aliquot of the solution for chemical analyses. The cell was mounted at a constant position, having 4.0 mm distance from the top surface of the oscillator. After bubbling the solution (10 mL) with Ar or He gas, sonication was conducted for 5 min–2 days. The reaction vessel

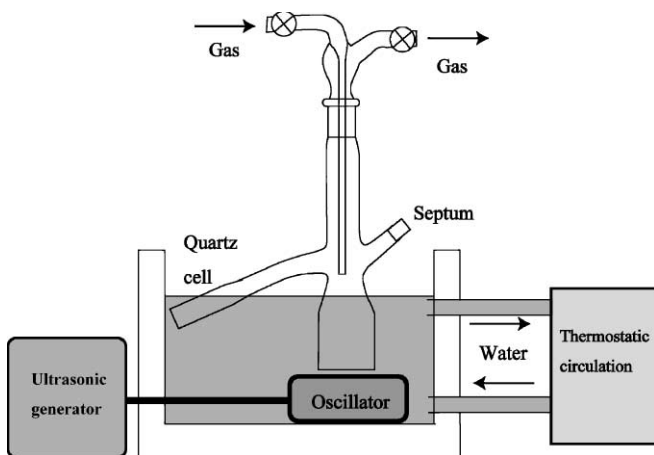


Fig. 1. A schematic view of the ultrasonic irradiation system.

was closed during the irradiation, and the temperature was kept at 20 °C controlled with a thermostatic circulation bath.

The concentration of  $^{99}\text{Tc}$  was determined from the radioactivity measured with a liquid scintillation counter (Aloka LSC-5100). UV-visible spectra were recorded on a Shimadzu MultiSpec-1500 in the range from 190 to 800 nm. The fraction of  $^{99}\text{TcO}_2 \cdot n\text{H}_2\text{O}$  colloids and  $\text{TcO}_4^-$  ions in the sample was determined by thin layer chromatography (TLC). TLC was performed using Merck 60 F254 precoated silica gel plate (0.2 mm in thickness). Radioactivity of  $^{99}\text{Tc}$  species on a TLC-plate was visualized with an imaging plate (Fuji Photo Film, BAS-IP SR 2025) analyzed with a Bio Imaging Analyzer (Fuji Photo Film, BAS-5000).

The formation rate of OH radicals during sonolysis of water was estimated by a method similar to Fricke dosimetry [14]. A 10 mL of Ar-saturated (and/or He) aqueous solution containing 50 mM  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$  and 0.8 M  $\text{H}_2\text{SO}_4$  was sonicated, and amounts of Fe(III) ions formed from the oxidation of Fe(II) by OH radicals were determined spectrophotometrically.

## Results and discussion

### Sonication of aqueous solution of $\text{TcO}_4^-$

In sonolysis of water molecules, H radicals as a reducing reagent should be produced primarily by cavitation phenomena. However, no reduction of Tc(VII) was observed by UV-vis spectrophotometry (Fig. 2) when aqueous  $\text{TcO}_4^-$  solutions were sonicated for 5 min–2 days under Ar atmosphere. This observation is different from the  $\gamma$ -radiolysis of  $\text{TcO}_4^-$  ions [4–6]; Tc(VII) was reduced *via* reduction processes triggered by hydrated electrons in neutral solutions and by H radicals in acidic solutions, resulting that Tc(IV) species were formed.

The reason why Tc(VII) was not reduced by sonolysis might be qualitatively explained as follows. A reduction reaction of Tc(VII) with H radicals is quite slow. The reaction rate previously determined,  $5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  [5], is much smaller than the oxidation rate of Tc(VI) by OH radicals [15],  $2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . In addition, it is taken into consideration that the radical reactions by sonolysis only

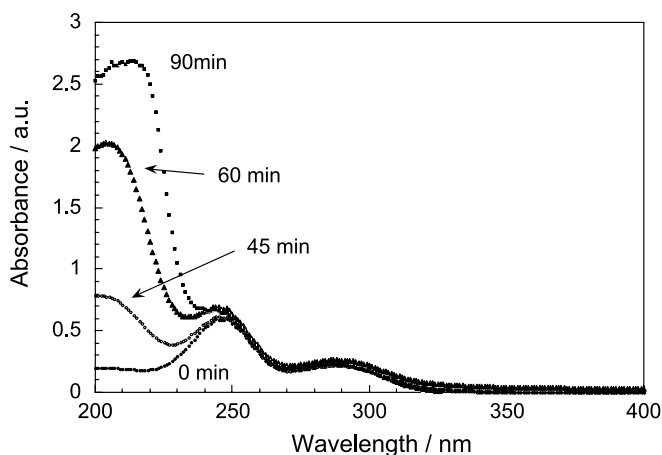


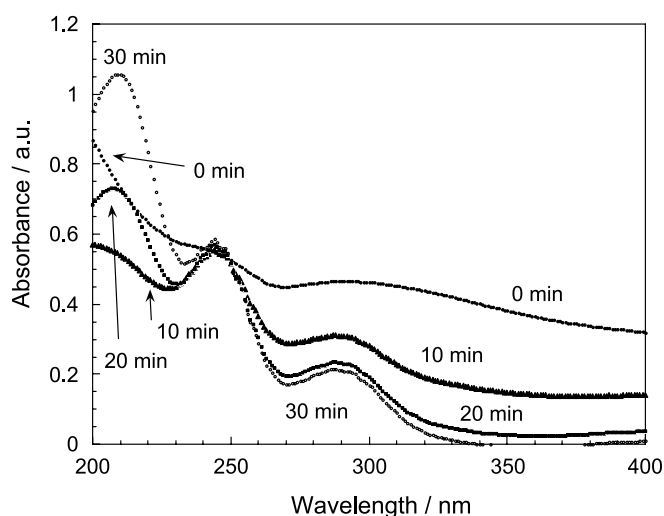
Fig. 2. Absorption spectra of the aqueous  $\text{TcO}_4^-$  solution depending on a sonication time. Sonication time is indicated in the figure. Absorption peaks at 245 nm and 287 nm are due to  $\text{TcO}_4^-$ .

take place in and around the cavitation bubbles, where concentrations of H and OH radicals are quite high. Thus, if Tc(VII) is reduced by H radicals and Tc(VI) is once formed, Tc(VI) should be immediately oxidized by OH radicals in its vicinity. This local reaction of the radicals can be consequently recognized as the efficient production of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). In Fig. 2 an absorption peak around 210 nm ( $\text{H}_2\text{O}_2$ ) quickly emerges with increasing sonication time, suggesting that the recombination reaction of OH radicals occurred effectively in the vicinity of the bubbles.

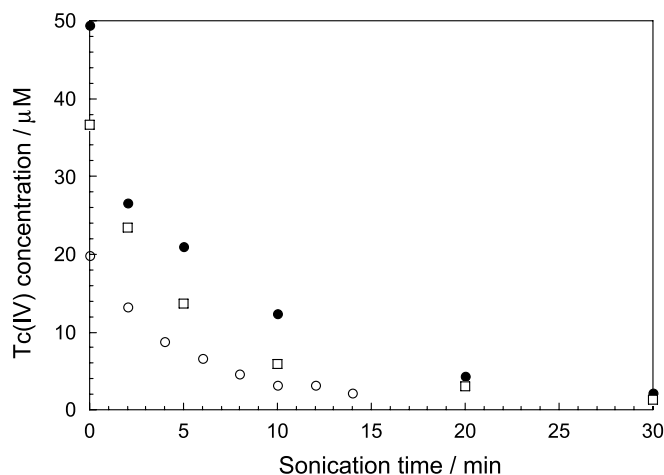
In contrast to sonolysis, radiolysis by  $\gamma$ -rays provides different conditions; it gives homogeneous distribution of the radicals in bulk solutions, and a production of hydrated electrons that reduce Tc(VII) effectively (a bimolecular reaction of  $\text{TcO}_4^-$  with  $e_{\text{aq}}^-$  with a reaction constant of  $10^{10} \text{ M}^{-1} \text{ s}^{-1}$  [15]). On the other hand, a high LET irradiation such as  $\alpha$  particles irradiation of Tc(IV) species resulted in the production of  $\text{TcO}_4^-$ , observed by Poineau *et al.* [10]. They pointed out that the radiolytic oxidation of Tc(IV) by  $\alpha$  particles irradiation occurred even under a reducing conditions and  $\text{H}_2\text{O}_2$  was involved in its oxidation processes. The enhancement of  $\text{H}_2\text{O}_2$  production is one of the characteristic phenomena in the case of high LET irradiations due to recombination reactions of OH radicals. This situation seems similar to the present sonolysis case where a production of  $\text{H}_2\text{O}_2$  was prominent and oxidation of Tc(IV) was observed as discussed below.

### Sonication of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ colloids solutions

Sonolysis of  $\text{TcO}_2 \cdot n\text{H}_2\text{O}$  colloids dispersed in aqueous solutions was investigated under Ar or He atmosphere. Gradual oxidation was observed from the  $\text{Tc(IV)O}_2 \cdot n\text{H}_2\text{O}$  colloids to  $\text{TcO}_4^-$  as shown in Fig. 3. The original brownish black color of the suspension disappeared leaving behind a colorless solution. The original suspension ( $t = 0$ ) showed continuous absorption spectra due to light scattering by colloid particles [4]. With an increase of sonication time, this broad background intensity decreased and the absorption peaks



**Fig. 3.** Sonication time dependence on the absorption spectra of the  $\text{TcO}_2 \cdot n\text{H}_2\text{O}$  colloids solutions. Sonication time is indicated in the figure. Absorption peaks at 245 nm and 287 nm are due to  $\text{TcO}_4^-$ .



**Fig. 4.** The concentration change of Tc(IV) against sonication time. Initial Tc(IV) concentration: ●  $5.0 \times 10^{-5} \text{ M}$  ×  $3.7 \times 10^{-5} \text{ M}$  ×  $2.0 \times 10^{-5} \text{ M}$ .

(245 nm and 287 nm) of  $\text{TcO}_4^-$  appeared. In Fig. 4, the concentration of Tc(IV) against sonication time was plotted as typical examples of experimental data in Ar. The oxidation of Tc(IV) was nearly completed in 30 min under Ar atmosphere. It took more than 30 min for a complete oxidation under He atmosphere. The sonochemical oxidation of  $\text{TcO}_2 \cdot n\text{H}_2\text{O}$  was depressed about 40% by the addition of 0.5 M *t*-butyl alcohol (an effective scavenger of OH radicals), indicating that Tc(IV) was oxidized by the attack of OH radicals.

It should be noted again that the rate of oxidation of Tc(IV) in Ar was larger than that in He. It was likely considered that Tc(IV) might be oxidized by trace oxygen in the solutions or the reaction vessel during sonication. However, our preliminary sonolysis experiments denied its possibility. We found that Tc(IV) in aerobic condition was oxidized slower than in Ar, and more or less faster than in He. This fact strongly suggests that the Tc(IV) oxidation was governed by sonolytic effects. The reaction kinetics is discussed for the data in noble gas atmosphere for simplicity in this paper, and analysis of the data in air will be discussed elsewhere.

### Kinetics of sonochemical oxidation of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$

Although various sonochemical reactions have already been reported, the kinetics for the reactions is still unclear. Analysis with a simple model with a first order reaction was failed to fit to the present data, and a heterogeneous reaction model proposed by Okitsu *et al.* [16] was examined.

The model is similar to a Langmuir-Hinshelwood mechanism or an Eley-Rideal mechanism which is often applied to a kinetic analysis of heterogeneous gas-solid catalytic reactions [17]. In this model, it is assumed that OH radicals exist in the interface region of the collapsing bubbles and then solute molecules react with OH radicals in this region. "An effective reaction site" is defined at the surrounding cavitation bubble. In addition, the equilibrium constant of solutes toward the effective reaction site,  $K$ , is defined in which solute molecules are concentrated or non-concentrated on the reaction site before the bubbles collapse. At the moment the bubbles collapse, it is assumed that solute

molecules react with OH radicals with a pseudo-rate constant of  $k$ .

The rate of adsorption of solute (X) molecules from the bulk solution to "the effective reaction site" around the cavitation bubbles is proportional to the concentration of solutes in the bulk solution and  $(1 - \theta)$ , where  $\theta$  corresponds to the ratio of solutes occupied in the effective reaction site. In addition, the rate of desorption is proportional to  $\theta$ . At equilibrium, the rates should be equal,

$$k_1[X](1 - \theta) = k_{-1}\theta, \quad (1)$$

where  $k_1$ ,  $k_{-1}$  are the rate constant for adsorption and for desorption, respectively, and  $K$  is defined as  $k_1/k_{-1}$ . Then,  $\theta$  is written as

$$\theta = \frac{K[X]}{1 + K[X]}. \quad (2)$$

When the solute molecules in the effective reaction site react with OH radicals, the reaction rate,  $r$  ( $\text{M s}^{-1}$ ), could be represented as

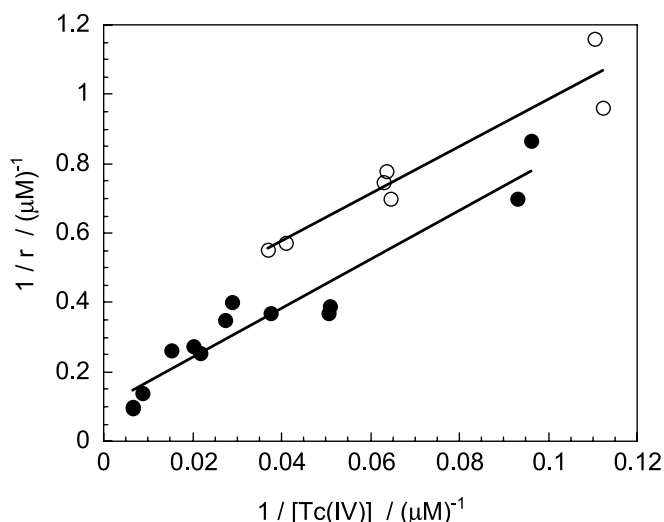
$$r = k\theta = \frac{kK[X]}{1 + K[X]}, \quad (3)$$

where  $k$  is the pseudo-rate constant for the reaction of solutes with OH radicals. Inverting both sides of Eq. (3) gives,

$$\frac{1}{r} = \frac{1}{kK} \frac{1}{[X]} + \frac{1}{k}. \quad (4)$$

The values of  $k$  and  $K$  for  $\text{TcO}_2 \cdot n\text{H}_2\text{O}$  can be determined by preparing a reciprocal plot of initial decomposition rate  $r$  (at sonication time  $t = 0$ ) of  $\text{TcO}_2 \cdot n\text{H}_2\text{O}$  versus initial concentration of  $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ . In the present case, the solute concentration  $[X]$  was taken as Tc(IV) monomer concentration for simplicity, as shown in Fig. 5. In both cases, a linear correlation was roughly obtained. Hence, it is said that the heterogeneous model of sonolysis reactions proposed by Okitsu *et al.* [16] can be applied to the present case.

Table 1 summarizes the rate constant ( $k$ ) and the equilibrium constant ( $K$ ) calculated from the straight lines in Fig. 5.



**Fig. 5.** Analysis of the kinetics of Tc(IV) oxidation by using Eq. (4). Reciprocal plot of initial rate of oxidation of Tc(IV) versus initial concentration of Tc(IV). □: He atmosphere, ●: Ar atmosphere.

**Table 1.** Pseudo-rate constants,  $k$ , and equilibrium constants,  $K$ , calculated on the basis of the heterogeneous model (Eq. (4)).

Saturating gas	$R^a$	$k$ , $\mu\text{M min}^{-1}$	$K$ , $\mu\text{M}^{-1}$
Helium	0.91	3.3	0.044
Argon	0.92	10.1	0.014

a: Correlation factor for fitting.

**Table 2.** Effects of saturating gases on OH formation rate.

Gas	OH formation rate, $\mu\text{M min}^{-1}$	Thermal conductivity, $\text{mW m}^{-1} \text{K}^{-1}$ (300 K) <sup>16</sup>	Polytropic index, $C_p/C_v$ (25 °C) <sup>16</sup>
Helium	$11.6 \pm 1.2$	156.7	1.67
Argon	$28.1 \pm 2.7$	17.9	1.68

The  $K$  values obtained in this experiment are smaller than unity, and it means that the rate of adsorption ( $k_1$ ) is smaller than the rate of desorption ( $k_{-1}$ ). On the other hands, the rate constant of Tc(IV) oxidation showed that the rate constant under Ar is three times higher than the rate constant under He. In order to understand the difference of the oxidation rates depending on the atmosphere, we tried to measure the formation rate of OH radicals as discussed below.

Formation rates of OH radicals in sonolysis of water were measured by using Fricke dosimetry [14] as used for radiolysis. From the yield of Fe(III) ions, the rate was estimated as  $28.1 \pm 2.7 \mu\text{M min}^{-1}$  under Ar, and  $11.6 \pm 1.2 \mu\text{M min}^{-1}$  under He, respectively (Table 2). The formation rate under Ar was almost three times higher than that under He, and this result explains the difference of the oxidation rate of Tc(IV) in different atmospheres well.

The OH-radical production yield depends on the nature of the operating gas. The temperature reached in the compressed bubble depends mainly on the ratio of specific heats  $C_p/C_v$  (polytropic index) of the gas and its thermal conductivity [18]. In simple adiabatic model, a final temperature  $T_f$  and a final volume  $V_f$  of the collapsed bubble are linked by the expression  $T_f/T_0 = (V_0/V_f)^{C_p/C_v-1}$ , where  $T_0$  and  $V_0$  are an initial temperature and an initial volume of the bubble. In the present case, the ratio  $C_p/C_v$  of He and Ar is almost the same (Table 2), because both are monoatomic gases. However, thermal conductivity of He is much higher than that of Ar (Table 2). The rate at which energy is transferred out of the bubble is expected to increase as the thermal conductivity of the gas increases. Thus, bubbles with He should be cooler than bubbles with Ar, resulting that the OH-radical yield under He should be lower than under Ar atmosphere. It is consistent with the experimental results that the oxidation reaction of Tc(IV) under Ar occur more rapidly than under He.

## Conclusion

We examined redox reactions of Tc(VII) and Tc(IV) by sonolysis comparing with the radiolysis results previously reported. Formation of Tc(IV) by reduction of Tc(VII) was observed in  $\gamma$ -radiolysis, while no reduction of Tc(VII) in

an aqueous solution was found in the case of sonolysis. On the contrary, Tc(IV) oxidation was occurred in sonolysis and Tc(VII) was eventually produced. It is concluded that OH radicals produced by cavitation phenomena played an important role on the oxidation of Tc(IV) in sonolysis. The oxidation rates of Tc(IV) under Ar atmosphere was three times higher than under He atmosphere. This is attributed to the difference of OH formation rates in cavitation bubbles caused by the difference of thermal conductivity of the gases.

*Acknowledgment.* The authors acknowledge to Prof. T. Ohtsuki and machine group members of the Laboratory for Nuclear Science, Tohoku University, for their assistance for bremsstrahlung irradiation. Financial support was provided by the Ministry of Education, Culture, Sports, Science and Technology, Japan (a Grant-in-Aid for Scientific Research No.18560800).

## References

1. Said, K. B., Seimbille, Y., Fattahi, M., Houee-Lévin, C., Abbé, J. C.: *Appl. Radiat. Isot.* **54**, 45 (2001).
2. Lukens Jr., W. W., Bucher, J. J., Edelstein, N. M., Shuh, D. K.: *Environ. Sci. Technol.* **36**, 1124 (2002).
3. Lukens Jr., W. W., Bucher, J. J., Edelstein, N. M., Shuh, D. K.: *J. Phys. Chem. A* **105**, 9611 (2001).
4. Sekine, T., Narushima, H., Kino, Y., Kudo, H., Lin, M., Katsumura, Y.: *Radiochim. Acta* **90**, 611 (2002).
5. Sekine, T., Narushima, H., Suzuki, T., Takayama, T., Kudo, H., Lin, M., Katsumura, Y.: *Colloids Surf. A: Physicochem. Eng. Aspects* **249**, 105 (2004).
6. Zakir, M., Sekine, T., Takayama, T., Kudo, H., Lin, M., Katsumura, Y.: *J. Nucl. Radiochem. Sci.* **6**, 243 (2005).
7. Vichot, L., Ouvrard, G., Montavon, G., Fattahi, M., Musikas, C., Grambow, B.: *Radiochim. Acta* **90**, 575 (2002).
8. Vichot, L., Fattahi, M., Musikas, C., Grambow, B.: *Radiochim. Acta* **91**, 263 (2003).
9. Fattahi, M., Vichot, L., Poineau, F., Houée-Levin, C., Grambow, B.: *Radiochim. Acta* **93**, 409 (2005).
10. Poineau, F., Fattahi, M., Grambow, B.: *J. Nucl. Radiochem. Sci.* **6**, 237 (2005).
11. Suslick, K. S.: *Science* **247**, 1439 (1990).
12. Flint, E. B., Suslick, S.: *Science* **253**, 1397 (1991).
13. McNamara III, W. B., Didenko, Y. T., Suslick, K.: *J. Phys. Chem. B* **107**, 7303 (2003).
14. Mizukoshi, Y., Oshima, R., Maeda, Y., Nagata, Y.: *Langmuir* **15**, 2733 (1999).
15. Pikaev, A. K., Kryuchkov, S. V., Kuzina, A. F., Spitsyn, A. V. I.: *Dokl. Akad. Nauk SSSR* **236**, 1155 (1977).
16. Okitsu, K., Iwasaki, K., Yobiko, Y., Bandow, H., Nishimura, R., Maeda, Y.: *Ultrason. Sonochem.* **12**, 255 (2005).
17. Atkins, P. W., Locke, J. W.: *Physical Chemistry*. Oxford University Press (1997), p. 999.
18. McNamara III, W. B., Didenko, Y. T., Suslick, K. S.: *Nature* **401**, 772 (1999).