10640 *J. Phys. Chem. A* **2007,** *111,* 10640−10645

Reactions of Radicals with Hydrolyzed Bi(III) Ions: A Pulse Radiolysis Study

R. Benoit and M.-L. Saboungi*

CRMD-CNRS, Université d'Orléans, 1b rue de la Férollerie, 45071 Orléans Cedex 2, France

M. Tréguer-Delapierre

ICMCB-CNRS, Université Bordeaux I, 87 avenue du Dr. Schweitzer, 33608 Pessac Cedex, France

B. H. Milosavljevic and D. Meisel*

The Radiation Laboratory and Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556

Received: May 20, 2007; In Final Form: July 27, 2007

Radiolytic reduction of $BiOClO_4$ in aqueous solutions leads to the formation of bismuth clusters and larger nanoparticles. The mechanisms of redox reactions of the polycationic Bi(III) species that exist in the solution were investigated with pulse radiolysis. The kinetic and spectral properties of the transients formed by the reaction of these species with the primary radicals from water radiolysis are reported. The single-electron reduction product, $Bi_9(OH)_{22}{}^{4+}$, absorbs at $\lambda_{max} = 273$ nm, while the OH adduct, $Bi_9(OH)_{23}{}^{5+}$, has a broad absorption spectrum with a maximum at 280 nm and a shoulder at 420 nm. Several rate constants were measured: $k\ (e^-_{aq} + Bi_9(OH)_{22}{}^{5+}) = 1.2 \times 10^{10}\ M^{-1}\ s^{-1}$ and $k\ (OH + Bi_9(OH)_{22}{}^{5+}) = 1.5 \times 10^9\ M^{-1}\ s^{-1}$. The reduced species, $Bi_9(OH)_{22}{}^{4+}$ further reacts with $(CH_3)_2COH$ radicals, but not with $CH_2C(CH_3)_2OH$ radicals from *t*-butanol, to produce a doubly reduced polynuclear species. A few reactions of the reduction of the Bi salt in the presence of poly(acrylic acid) are also described. In the presence of the polymer, a metal−polymer complex is formed prior to the irradiation, and the reduction reactions are significantly slowed down.

Introduction

In the search for highly efficient thermoelectric materials, it was recently discovered that nanomaterials, particularly quantum dots, offer opportunities for enhancing the figure of merit, $ZT = S^2\sigma T/\kappa$, where S, σ, T, and κ are the Seebeck coefficient, the electrical conductivity, the working temperature, and the thermal conductivity, respectively.[1,2] Bismuth is a very attractive material for thermoelectric applications since it is a semimetal characterized by high electron mobility, long mean free paths, and heavy effective masses.[3] It has been also associated with the discovery of several transport phenomena, including the Hall, Seebeck, Nernst, and Ettinghausen effects. Before the advent of silicon and germanium semiconductors, bismuth was used to investigate the effects of doping. Its electronic and transport properties are extremely sensitive to magnetic fields, and its very large magnetoresistance was discovered by Kapitza[4] early in the 1920s. Since these electronic properties depend on the degree of overlap of the valence and conduction bands, which respond in different ways to the effects of confinement, there has been considerable interest in the effects of reduced dimension on these phenomena. A semimetal-to-semiconductor transition has been reported in Bi thin films,[5] and Dresselhaus, Heremans, and collaborators have studied arrays of Bi nanowires and found dramatic changes in the thermoelectric[6,7] and electronic[8] transport properties. Recent studies have shown that Bi quantum dots embedded in a superlattice structure can achieve a large effective thermoelectric figure of merit ($ZT > 5$).[9] While, from a theoretical standpoint, elemental Bi appears to be one of the best thermoelectric materials, it is still challenging if not impossible to control the synthesis and to stabilize Bi quantum dots in solution at dimensions below 10 nm.[10,11] The best results so far have been obtained by capping the nanoparticles with polymers, but this modifies the surface of the material and prevents carrier filtering by electrical conductivity. Here, we propose a new approach to stabilizing Bi nanoparticles inside mesoporous silica based on γ radiation of Bi salt solutions. Quantum dots embedded in a host material introduce many interfaces that can reduce the thermal conductivity and enhance the carrier energy filtering by thermionic emission.[12] To that end, we initiated a study of the mechanisms and kinetics of the reduction of Bi salts in aqueous solution by pulse radiolysis with and without a polymeric stabilizer. It has already been demonstrated that partially hydrolyzed Bi(III) forms Bi nanoparticles upon radiolytic reduction in aqueous solutions.[13] The pulse radiolysis technique enables one to obtain insight into the early reduction stages of the ionic Bi precursor and the stability of the unusual valence oxidation states of the Bi intermediates. In particular, we focus on Bi(III) polynuclear oxy/hydroxide complexes, since they contain several Bi centers, which, upon reduction, might act as nucleation centers for growth of the particles. Very little is presently known about these processes. Pulse radiolysis studies have been performed on aqueous Bi(III) solutions in highly concentrated hydrochloric and perchloric acids.[14,15] The oxidation of Bi^{3+} by OH radicals and its reduction by H atoms and alcohol radicals were measured in these concentrated acidic media. Similar studies on the oxidation of aqueous polyselenide solutions by pulse radiolysis eventually

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* Corresponding author. E-mail: mls@cnrs-orleans.fr (M.-L.S.); dani@nd.edu (D.M.).

10.1021/jp073895b CCC: $37.00

led to the radiolytic production of selenium nanoparticles, a very difficult synthesis by any other method.[16]

In the present work we have studied the time evolution of the radiolytically induced reduction of hydrolyzed Bi(III) in aqueous solution and its parallel reactions with OH radicals. We also performed experiments in which the reduction was carried out in the presence of the commonly used poly(acrylic acid) (PAA) stabilizer. The selected starting salt was bismuthyl perchlorate ($BiOClO_4$) in water near its natural pH. Under these conditions, $BiOClO_4$ is known to hydrolyze to a large extent into aquated complexes within a few minutes at ambient temperature. The hydrolysis leads to the formation of mono- and polynuclear species in rather complex processes that have been thoroughly studied.[17−19] The degree of hydrolysis of the ionic precursor and the species formed are strongly dependent on the pH of the solution and on the BiO^+ concentration. At medium to high concentrations of Bi (10^{-4}−0.5 M) and in strongly acidic media (pH < 1), the Bi^{3+} ions have been identified as the major species. When the pH increases beyond 1, mononuclear $BiOH^{2+}$ and $Bi(OH)_2^+$ species form and rapidly polymerize into polynuclear species with the general formula $(BiO)_n^{n+}$ or $Bi_n(OH)_{2n}^{n+}$. The most commonly observed complex is the hexanuclear ion $Bi_6(OH)_{12}^{6+}$, which exists over a wide range of solution compositions.[20] Upon further increase of the pH, products of a higher degree of condensation, such as $Bi_9(OH)_{21}^{6+}$ and $Bi_9(OH)_{22}^{5+}$, have been identified. For a ratio of $[OH^-]/[Bi(III)] > 2.44$, the complexes become insoluble and precipitate.[21] Most of the experiments in the present study were performed in an acidic range (pH 3−5) and $[BiOClO_4] = (0.3-3.8) \times 10^{-3}$ M. As a result, complexes with a high positive charge, primarily $Bi_9(OH)_{22}^{5+}$, are the dominant species present in the solution prior to the irradiation.

Experimental Section

All the chemicals used ($BiOClO_4$, 2-propanol, *t*-butanol, PAA of an average molecular weight of 2 400 000) were of the highest purity commercially available from Aldrich or Acros. All measurements were conducted with fresh solutions prepared immediately prior to irradiation. The solutions were continuously deaerated by bubbling nitrogen or nitrous oxide through them for at least 30 min before irradiation until the end of experiment. The radiation cell was connected to an apparatus that renewed the irradiated solution after each pulse in order to prevent stable radiolysis products from accumulating in the cell. When necessary, their pH was adjusted with potassium hydroxide. Pulse radiolysis experiments were performed using 2-ns pulses of 8 MeV electrons from the Notre Dame Radiation Laboratory linear accelerator (TB-8/16-1S linac). Details of the linac, the spectrophotometric detection setup, and the computer-controlled data acquisition are described elsewhere.[22] All measurements were performed in a 1-cm optical path high-purity quartz cell. The concentration of radicals generated by the pulse was approximately 2×10^{-6} M per pulse as determined by a thiocyanate dosimeter.

Results

Aqueous Solutions without Stabilizers. The difference−absorption spectra of the transients observed following pulse irradiation of a 0.9×10^{-3} M $BiOClO_4$ solution at pH = 3.4 are shown in Figure 1. In the N_2-saturated solution, the spectrum exhibits a maximum at ∼280 nm and a shoulder around 420 nm; all the radicals from water radiolysis, e^-_{aq}, OH, and H react with the Bi(III) species. In N_2-saturated solutions, the observed spectrum is thus a superposition of the spectra of the products formed from reactions with these three radicals. By scavenging the OH radicals with 0.1 M *t*-butanol, the absorption around 420 nm is significantly diminished, while that at 280 nm diminishes less. The transient absorption is due solely to the reduced products, primarily from the reaction with e^-_{aq} with a small contribution from the H atom reaction. On the other hand, in N_2O-saturated solutions, where e^-_{aq} is converted to OH radicals, the intensity of the peak at 280 nm increases, and the one of the shoulders around 420 nm almost doubles. These observations indicate that the reaction of the initial polynuclear species, $Bi_9(OH)_{22}^{5+}$, with OH radicals produces an intermediate that has an absorption band around 280 nm and a shoulder at 420 nm. On the other hand, the reduced species formed by the reaction of e^-_{aq} and H atoms absorbs primarily in the 273 nm region. Because of the contribution from both the reduced and oxidized products to the absorption in the 270−280 region, the increase in the absorption upon conversion of e^-_{aq} to OH (N_2O saturation) in that range is not as pronounced as it is in the 420 nm range.

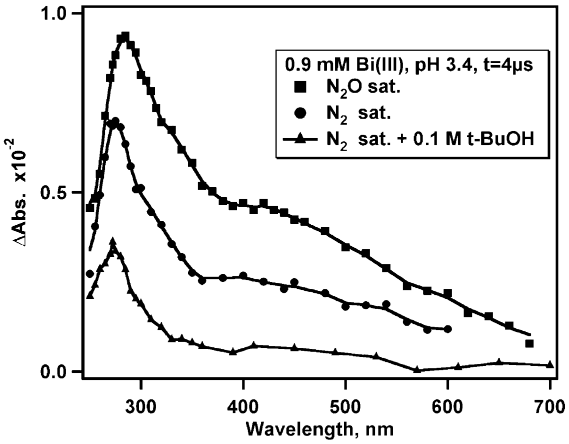

Figure 1. Difference−absorption spectra of the Bi(III) species obtained 4 μs after pulse-irradiation of 0.9×10^{-3} M $BiOClO_4$ solutions at pH = 3.4 saturated with N_2 (circles), N_2O (squares), and N_2 containing 0.1 M *t*-BuOH (triangles).

Under the experimental conditions of Figure 1, all the reactions discussed above are over within 3.5 μs following the pulse. In order to verify the possible role of H atoms in the reduction of $Bi_9(OH)_{22}^{5+}$, e^-_{aq} radicals were scavenged by adding N_2O in solutions containing 0.1 M *t*-BuOH, so that H atoms remain the only radicals available for reduction (not shown in Figure 1). A weak absorption band peaking at 275 nm was observed, in agreement with the suggestion that H atoms are able to reduce $Bi_9(OH)_{22}^{5+}$ to produce a product absorbing in this region. The similarity in the absorption spectra of the products from the H atoms and the hydrated electrons suggest that both generate the same intermediate. Thus the absorption band with a maximum at 275 nm is attributed to the reduced, mixed-valence species $Bi_9(OH)_{22}^{4+}$. The molar extinction coefficient of this product, calculated assuming that $G(e^-_{aq} + H) = 3.2$ radicals/100 eV, is $\epsilon = 4000\ M^{-1}\ cm^{-1}$.

In contrast to the spectrum of the reduced form, the spectrum of the OH reaction product exhibits a maximum at 280 nm and a shoulder at 420 nm. A Bi(IV) oxidation product is expected to be further hydrolyzed than the III-valence precursor. We therefore assign the product of the reaction with OH radicals formally to a Bi(III)/Bi(IV) mixed-valence OH adduct, rather than to a direct electron-transfer oxidation product. The absorption spectrum of this $Bi_9(OH)_{23}^{5+}$ adduct was deduced from the spectrum collected in N_2O-saturated solutions by subtracting the small contribution of $Bi_9(OH)_{22}^{4+}$ produced by reduction

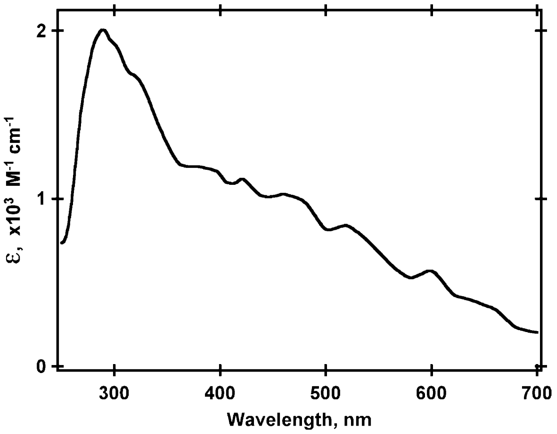

Figure 2. Corrected absorption spectrum of $Bi_9(OH)_{23}^{5+}$.

by H atoms (determined in solutions containing 0.1 *t*-butanol and saturated with N_2O, and thus only H atoms). The spectrum of the OH reaction product, corrected for the small contribution from H atoms (but not for the spectrum of the depleted parent complex), is shown in Figure 2, where the extinction coefficients have been computed using the commonly accepted yields $G(OH) = 2.7$, $G(e^-_{aq}) = 2.7$, and $G(H) = 0.5$ molecules/100 eV of absorbed energy. At the wavelength of maximum absorption (280 nm), the extinction coefficient of the adduct is $\epsilon = 2040$ M^{-1} cm^{-1} (see Figure 2).

The rate constants of the reactions of e^-_{aq} and H atoms with $Bi_9(OH)_{22}^{5+}$ were determined from the rate of the disappearance of e^-_{aq} at 700 nm and the rate of formation of the reduced species $Bi_9(OH)_{22}^{4+}$ at 290 nm. In all cases, the observed rates followed a pseudo-first-order rate law. The corresponding second-order rate constants were calculated from the dependence of the pseudo-first-order rates on Bi(III) concentration. In this system, reactions 1−4 dominate the kinetics of the intermediates:

$$H_2O \rightarrow e^-_{aq}, OH, H\ (H_2, H_2O_2) \tag{1}$$

$$e^-_{aq} + H_3O^+ \rightarrow H + H_2O \tag{2}$$

$$\text{Bi(III) (from } Bi_9(OH)_{21}^{6+} \text{ to } Bi_9(OH)_{22}^{5+}) + e^-_{aq} \rightarrow \text{Bi(II)} \tag{3}$$

$$\text{Bi(III)} + H \rightarrow \text{Bi(II)} + H^+ \tag{4}$$

Under the experimental conditions of this study (pH = 3−5), reactions 2 and 3 compete for the hydrated electrons. The contribution of reaction 2 was subtracted from the decay rate of e^-_{aq} using the well-established value $k_2 = 2.3 \times 10^{10}$ M^{-1} s^{-1}.[23] At pH 3.4, we obtain $k_3 = 1.1 \times 10^{10}$ M^{-1} s^{-1} for reaction 3, close to the value reported in the literature.[10] The rate constant depends weakly on pH, decreasing from 1.2×10^{10} to 0.85×10^{10} M^{-1} s^{-1} as the pH increases from 3 to 5. This decrease in rate constant is attributed to the shift in the hydrolysis products. The dominant parent polynuclear species present in solution become less positively charged as the pH increases, from $Bi_9(OH)_{21}^{6+}$ at pH 3.4 to $Bi_9(OH)_{22}^{5+}$ at pH 5. Considering the high positive charge on the complexes, these rate constants are believed to be slower than the diffusion-controlled limit.

The rate constant of the reaction of H atoms with $Bi_9(OH)_{22}^{5+}$ was obtained from experiments performed in the presence of *t*-butanol and N_2O, which scavenge OH radicals and e^-_{aq}, respectively. Thus H atoms, either directly from water radiolysis or from the faster reaction 2, contribute to reaction 4. The growth of $Bi_9(OH)_{22}^{4+}$ was followed near its absorption maximum at 273 nm, and the rate constant for reaction 4 was determined to be $k\ (Bi_9(OH)_{22}^{5+} + H) = 0.9 \times 10^{10}$ M^{-1} s^{-1}. This is a high rate constant for reduction by H atoms: we speculate that it indicates that the reaction involves neutralization of one of the Bi-bound hydroxide ions and thus requires only minimal reorganization energy. The high reorganization energy involved in reduction by the small H atom is commonly believed to be responsible for the sluggish reduction by this species. However, this determination is subject to a large experimental error because of the poor signal/noise ratio involved.

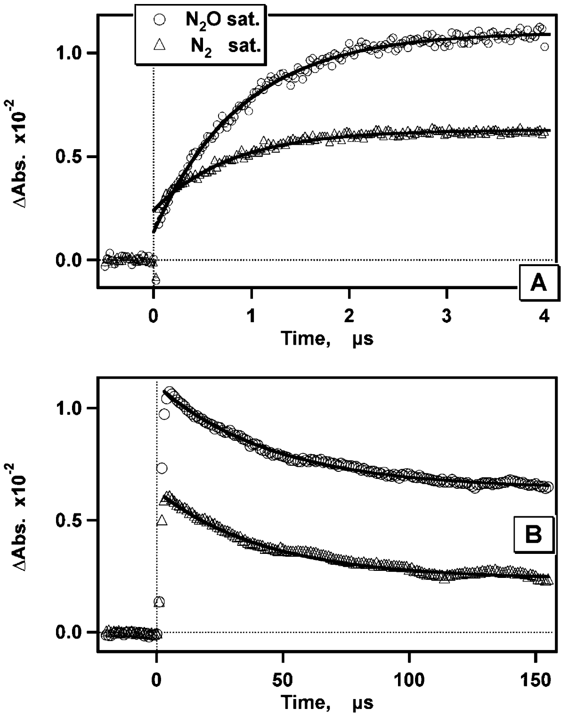

Figure 3. Formation (A) and decay (B) of absorption at 290 nm by $Bi_9(OH)_{23}^{5+}$ following a 2-ns pulse in N_2O (circles) or/and N_2 (triangles) saturated solutions containing 9×10^{-4} M Bi(III) at pH 3.4. The initial absorption in panel A is due to residual e^-_{aq}.

The rate constant of the reaction of OH radicals with $Bi_9(OH)_{22}^{5+}$ was determined in N_2O-saturated solutions at pH = 3.4−3.8 by following the increase in absorption at 290 nm. Under these conditions, essentially all the e^-_{aq} radicals are converted to OH, producing the OH adduct discussed above:

$$Bi_9(OH)_{22}^{5+} + OH \rightarrow Bi_9(OH)_{23}^{5+} \tag{5}$$

Figure 3A shows the increase in absorption at 290 nm as the OH adduct is formed in N_2O- and N_2-saturated solutions. The ratio of absorption at the end of the reaction in the two solutions quantitatively reflects the increase in OH concentration in the N_2O-saturated solution. The growth follows a pseudo first-order law, and the rate is proportional to the concentration of $Bi_9(OH)_{22}^{5+}$, leading to the second-order rate constant, $k\ (Bi_9(OH)_{22}^{5+} + OH) = (1.5 \pm 0.3) \times 10^9$ M^{-1} s^{-1}. The large uncertainty indicated for this rate constant is not due to experimental error but reflects changes in the hydrolyzed Bi (III) species as the concentration increases in the range of $(0.3-1) \times 10^{-3}$ M and the pH decreases from 3.8 to 3.4.

The OH adduct decays over a few hundred microseconds (Figure 3B) with $k = (3.0 \pm 0.3) \times 10^4$ s^{-1}. The rate of disappearance of $Bi_9(OH)_{23}^{5+}$ is described by a first-order kinetic rate law, independent of concentration in the range from 4×10^{-4} to 9×10^{-4} M as well as dose in the range from 0.7 to 2.5 krad. This independence of dose and concentration is

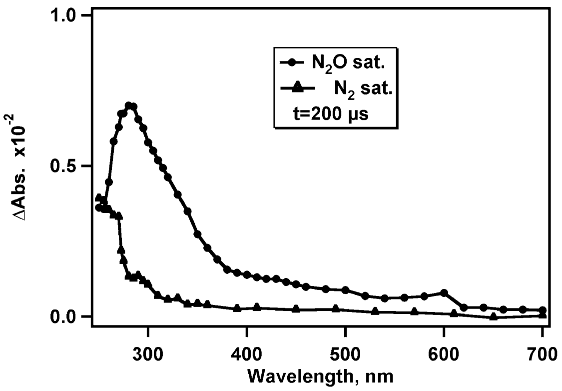

Figure 4. Difference absorption spectra of the product of the reaction of Bi(III) at pH 3.4 with OH (N_2O-saturated, circles) and e^-_{aq} + H (N_2-saturated containing 0.1 M *t*-butanol, triangles), recorded 200 μs after the pulse.

consistent with a unimolecular reaction of $Bi_9(OH)_{23}{}^{5+}$ with water or with H^+. The release of hydroxide ions,

$$Bi_9(OH)_{23}{}^{5+} + H_2O \leftrightarrow Bi_9(OH)_{24}{}^{4+} + H^+ \qquad (6)$$

is less likely considering the increase in the formal oxidation state of Bi. As can be seen in Figure 3B, the product of this decay reaction is a long-lived intermediate that remains in the solution beyond the time scale studied here, well into the millisecond time regime.

Figure 4 shows the spectra of the transients produced in both oxidizing and reducing environments 200 μs after the pulse. In N_2O-saturated solutions, the decay of the adduct $Bi_9(OH)_{23}{}^{5+}$ is essentially complete at this time, and the product, for example, of reaction 6 dominates. Its overall absorption in the whole UV–vis range has significantly decreased (compare with Figure 1 at 4 μs), but the shape of the spectrum did not change much. This can be attributed to the pH-dependent equilibrium state of the adduct hydrolysis (reaction 6), and the observed spectrum is then essentially that of an equilibrium concentration of the adduct and the hydrolyzed form.

In contrast to the product from the reaction with OH, the reduced transient $Bi_9(OH)_{22}{}^{4+}$ produced in the reducing environment from e^-_{aq} and H atoms in the presence of *t*-butanol remains stable for several hundred microseconds after the pulse. The amount of $Bi_9(OH)_{22}{}^{4+}$ hardly changes for at least 200 μs after the pulse in the presence of 0.1 M *t*-butanol in N_2-saturated solutions. However, when *t*-butanol is replaced by 2-propanol, which scavenges both OH radicals and H atoms, leading to the formation to the strongly reducing 1-hydroxy-1-methylethyl radical, the fate of the $Bi_9(OH)_{22}{}^{4+}$ changes. Under these conditions, the lifetime of the latter decreases considerably, its absorption decays rapidly, and a new absorption band develops around 380 nm (Figure 5). The rate of formation of this band follows a second-order rate law, increases with dose, and is essentially the same as the rate of the decay of the absorption at 273 nm. At an initial concentration of reducing radical $[(CH_3)_2COH] = 2 \times 10^{-6}$ M and an equal concentration of the reduced $Bi_9(OH)_{22}{}^{4+}$, the half-life of the radicals is 37 μs, corresponding to a rate constant of 1.3×10^{10} M^{-1} s^{-1}. Among the two possibilities, reduction by the radical or addition to the complex, we propose that this reaction is a further reduction of $Bi_9(OH)_{22}{}^{4+}$ by the organic radicals. The radical for 2-propanol appears to be sufficiently efficient as a reducing agent ($E° = -1.8$ V)[24] to react with $Bi_9(OH)_{22}{}^{4+}$ (reactions 7 and 8) at a diffusion-controlled rate. On the other hand, the addition reaction of the radical to form a $Bi_9(OH)_{22}{}^{4+}$ complex is expected to be independent of its redox potential and thus would have been observed with the *t*-butanol radicals as well:

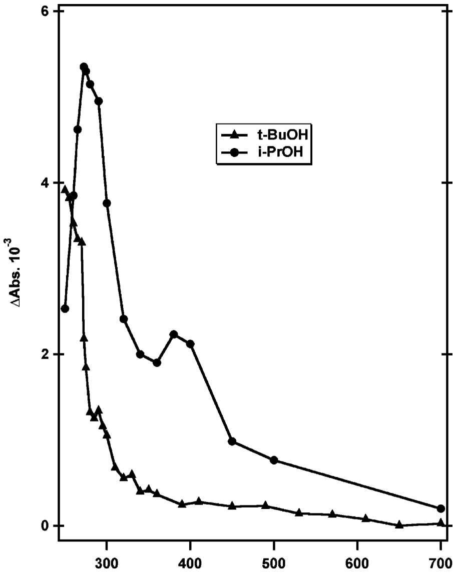

Figure 5. Difference absorption spectrum of the product of the reaction of Bi(III) with the $(CH_3)_2COH$ radicals from 2-propanol (circles). The solutions were N_2-saturated containing 0.1 M 2-propanol at pH 5 and recorded 150 μs after the pulse. For comparison, triangles show results of the equivalent *t*-butanol solutions from Figure 4.

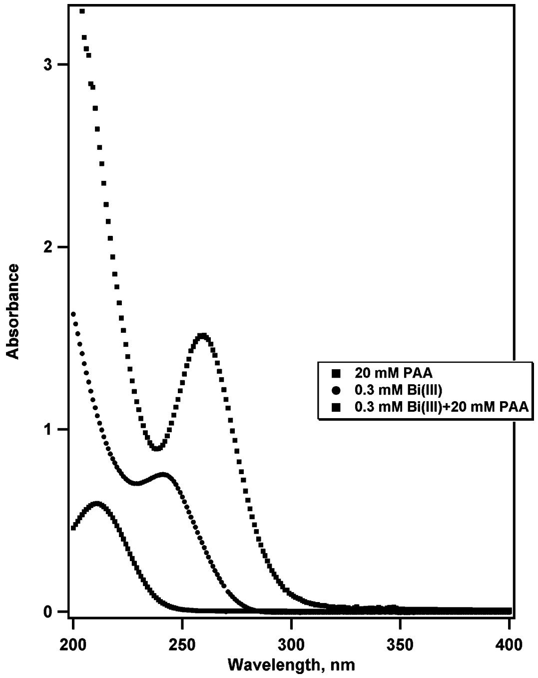

Figure 6. Effect of PAA on the absorption spectrum of $Bi_9(OH)_{22}{}^{5+}$ at pH 3.2 for different concentrations.

$$(CH_3)_2CHOH + OH\ (H) \rightarrow (CH_3)_2COH + H_2O\ (+H_2) \qquad (7)$$

$$Bi_9(OH)_{22}{}^{4+} + (CH_3)_2COH \rightarrow Bi_9(OH)_{22}{}^{3+} + (CH_3)_2CO + H^+ \qquad (8)$$

Effect of a Polymeric Stabilizer. The addition of PAA to the aqueous solution of Bi(III) increases the absorption by the polynuclear species $Bi_9(OH)_{22}{}^{5+}$ and shifts it to longer wave-

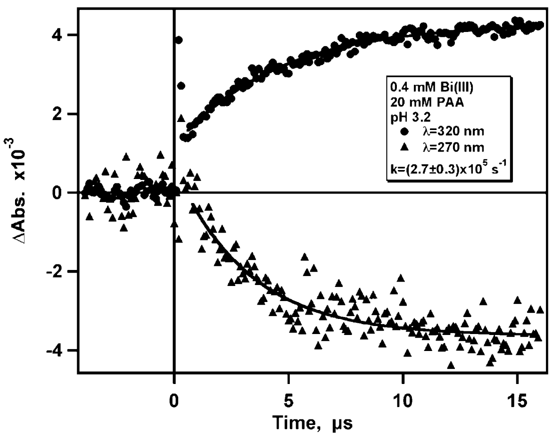

Figure 7. Rate of absorption increase due to reduction of a PAA−Bi(III) solution at 320 nm (circles) and due to its bleaching at 270 nm (triangles). Solid curves are fits giving the first-order rate constant.

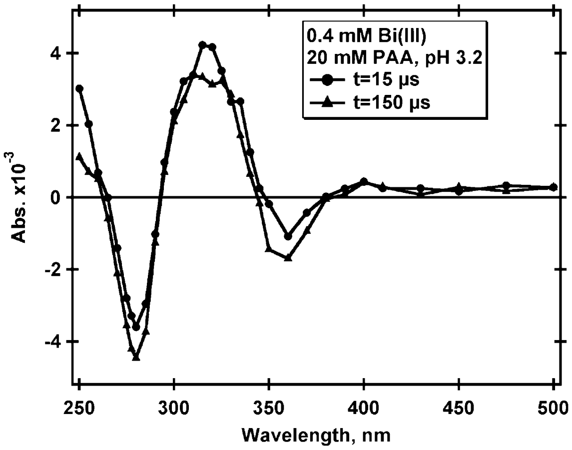

Figure 8. Difference absorption spectra following irradiation of the solutions of Figure 7 taken at $t = 15$ and 150 ms after the pulse.

lengths. A strong band can then be observed in the range 250−270 nm (Figure 6). These new features can be ascribed to the polyacrylate polymer interaction with the polynuclear Bi species. The extinction coefficient at 260 nm, the wavelength of maximum absorption under the conditions of Figure 6, is 5000 M^{-1} cm^{-1}. The spectra are highly sensitive to the pH: in acidic media (pH < 3), the 270 nm band is hardly observable, presumably because of protonation of the PAA, which shifts the equilibrium away from the PAA complex, while, in basic solutions, the formation of the Bi(III)-PAA complex is hindered by the formation of long polynuclear chains of the hydrolyzed Bi(III), which eventually precipitate out of solution. Similar complexation has been observed for other metal ions.[25]

When a 0.4×10^{-3} M $BiOClO_4$ solution containing 2.0×10^{-2} M PAA and 0.1 M *t*-butanol at pH 3.2 was pulse-irradiated, a rapidly increasing absorption at 320 nm concomitant with bleaching at the same rate at 270 nm was observed (Figure 7). The PAA polymer is mostly protonated to $PAAH^+$, and a large fraction of the hydrated electrons (e^-_{aq}) then reacts with H^+ or $PAAH^+$ to produce H atoms:

$$PAAH^+ \text{ or } H^+ + e^-_{aq} \rightarrow PAA + H \qquad (9)$$

The second-order rate constant of the latter in reaction with the Bi(III)−PAA complex was calculated from the results of Figure 7 to be $(6.7 \pm 0.7) \times 10^8$ M^{-1} s^{-1}.

The rate constant of the reaction between OH radicals and the polymer at pH = 3 was previously determined to be 9×10^7 M^{-1} s^{-1},[26] while that with *t*-butanol is 6×10^8 M^{-1} s^{-1}, so the reaction with *t*-butanol dominates. Accordingly, the 320 nm absorption band appearing in the microsecond range is assigned to reduced $Bi_9(OH)_{22}^{4+}$ complexed with PAA, produced in the H atom reaction. The spectrum of this species is shown in Figure 8. The decrease in the rate of the reduction of the complex by H atoms caused by the stabilizer is probably due to the slower diffusion of the complex relative to the free Bi(III) ion and by the lower driving force expected for the complexed ion relative to the free one. The reduction potential of the PAA−Bi(III) complex is expected to be more positive than that of the free ion because of the smaller stability constant of the reduced ion in the complex. No decay of PAA−$Bi_9(OH)_{22}^{4+}$ was detected within 200 μs.

Conclusion

The reactivity of hydrolyzed Bi polynuclear ions has been studied by time-resolved pulse radiolysis. Both free ions in solution and ions complexed to polyacrylate ions were included in the investigation. This technique makes it possible to observe the reactivity of polynuclear ions and determine their nuclearity-dependent properties during growth. These are important for understanding the growth mechanisms of the ions in both the radiation-induced and chemical reduction processes. The hydrolyzed Bi polynuclear ions are reduced by both hydrated electrons and H atoms, while OH addition dominates in the pH range 3.2−5. The reduced species, in which Bi is in an unusual and unstable oxidation state (+II), is long-lived (more than tens of microseconds, depending on the composition of the solution) within the framework of a mixed valence system. With the addition of alcohol, further reduction occurs because of the secondary-alcohol radicals. The species formed by the OH radical decays via unimolecular reaction with water. A PAA polymer environment slows down the kinetics of the reduction process but increases the stability of the transients against oxidation.

The motivation for this study stemmed from the ability to radiolytically reduce Bi(III) all the way to the elemental oxidation state and produce Bi nanoparticles.[27] The preexisting polynuclear complexes provide nucleation centers around which further clustering can occur. At the lowest concentrations of Bi(III) used, a significant reduction in the initial concentration of complexes must occur, especially after repetitive pulsing. Yet no effect on the kinetics of the initial redox reactions could be observed. Apparently, the initial high positive charge on the Bi(III) complexes and the electrostatic screening induced by the relatively ionic strength minimize these effects and allow the reduction (oxidation) reaction to proceed at essentially the same rate.

Acknowledgment. Support by the Centre National de la Recherche Scientifique (France) and the Office of Basic Energy Sciences, U.S. Department of Energy, is gratefully acknowledged. We thank Jean Etourneau (ICMCB) for many discussions. This is document NDRL No. 4684 from the Notre Dame Radiation Laboratory.

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