

Oscillatory Reactions $\text{Am(VI)} \rightleftharpoons \text{Am(V)}$ under Ozonation of Am(OH)_3 Suspension in Bicarbonate Solution

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Abstract—During prolonged ozonation of Am(III) hydroxide in bicarbonate solutions, oscillatory $\text{Am(VI)} \rightleftharpoons \text{Am(IV)}$ reactions were observed. Substitution of ^{241}Am with ^{243}Am , which is characterized by substantially lower specific radioactivity, does not change the character and parameters of the oscillatory process: the yields of ^{241}Am and ^{243}Am , and the oscillation period of about 2 min do not differ noticeably. The results suggest that the reductants in the system mainly originate from the ozone decomposition products; the arising hydroperoxy radicals and hydrogen peroxide partially reduce Am(VI) in the solution. The Am(VI) yield in ozonation of the Am(OH)_3 suspension in a bicarbonate solution substantially decreases with increasing the initial americium content.

It is known that ozonation of Am(OH)_3 suspension in bicarbonate solutions is the best method of preparing Am(VI) solutions [1, 2]. However, the kinetic characteristics, the effect of various factors on the Am(VI) yield, and the mechanism of this reaction have not been studied up to now. The goal of this work was to obtain the detailed information on the above reaction.

EXPERIMENTAL

In all the experiments, we used $^{241}\text{Am(OH)}_3$ or $^{243}\text{Am(OH)}_3$ obtained by addition of 1 M NaOH to neutral $\text{Am(NO}_3)_3$ solutions. An Am(OH)_3 precipitate was coagulated for 10 min, washed with water to neutral reaction, and then 4 ml of 0.12 M NaHCO_3 was introduced. The resulting aqueous suspension containing 0.2–1 mg of Am hydroxide was placed into a glass bubbler, and an ozone–oxygen mixture with 3.5% O_3 content (generated by a high-frequency ozonizer produced by Tekhnozon company, Russia) was passed through it at 20°C with 5–7 l h^{-1} flow rate. At regular intervals, ozonation was interrupted, and Am-containing mixture was transferred into a plastic tube with a capillary. After 10-min centrifuging at 8000g, the solution was placed into a 1-cm optical cell, and its absorption spectrum was recorded within the 300–1200 nm range on a Shimadzu-UV-160 spectrophotometer (Japan).

Ultrapure grade NaOH, NaHCO_3 , and HNO_3 were used.

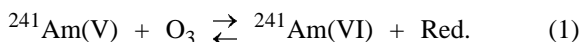
RESULTS AND DISCUSSION

After passing ozone–oxygen mixture through a $^{241}\text{Am(OH)}_3$ suspension in 0.12 M aqueous NaHCO_3 for several minutes, the solution acquires a reddish tint. In the absorption spectrum, the band at 503 nm belonging to the hydrated cation $\text{Am}^{3+} \cdot n\text{H}_2\text{O}$ disappears already after oxidation for 4 min, and the precipitate dissolves. In the process, the optical density of the solution grows within the 300–600 nm range, characteristic for Am(IV) in carbonate media [3] (Fig. 1, curves 1, 2). Further ozonation causes the optical density in this spectral region to decrease; after 15 min of ozonation, it decreases by a factor of 2 (curve 3). This fact can be attributed to Am(IV) oxidation to Am(V), whose ions do not absorb the light at 300–600 nm, in agreement with data of [3]. Then, at further ozonation, the absorption increases again, and after ~60 min only one band at 370 nm characteristic for Am(VI) [3] is observed (curves 4–7).

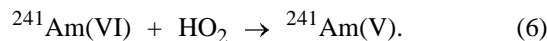
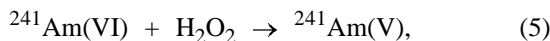
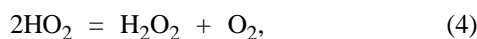
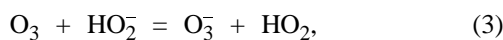
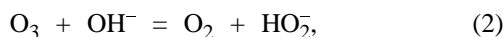
These data suggest that in bicarbonate solution Am(III) is oxidized with ozone at room temperature successively with formation of Am(IV), Am(V), and then Am(VI). It should be noted that the solution ozonized for several minutes acquires a strong reddish-brown color. The color does not change visually in time in spite of the above changes in the absorption spectrum. This fact, similarity of Am(IV) and Am(VI) spectra in bicarbonate solutions, and rapid dissolution of the Am(OH)_3 precipitate can lead to wrong conclusions when such a phenomenon will be considered as stabilization of americium in the hexavalent state.

In prolonged ozonation of the Am(VI) solution (>60 min), oscillations of intensity of the absorption band at 370 nm are observed, suggesting that the Am(VI) concentration periodically changes between the upper and lower extremal points (curves 1–12). The oscillation period found by us in special experiments amounts to ≤ 2 min. These oscillations occur only at ozone bubbling through the solution. After O_3 bubbling was stopped at any instant, the Am(VI) concentration did not change, and the system was stabilized for a long time. The maximal Am(VI) yield in the upper point was 95–96% from the initial americium content in the reaction system.

The mechanism of the oscillation process may be represented as follows. Dissolved ozone reacts with the lower valence state of americium to form Am(VI) until a sufficient amount of reductants is accumulated in the solution, and the rate of their reaction with Am(VI) becomes higher than the rate of its formation. Then, the reaction occurs in the reverse direction, and Am(VI) reduction to Am(V) is observed. In the course of reductant (Red) consumption in the reaction with Am(VI) , its concentration decreases to a value corresponding to the point when the rate of the reaction of reduced americium species with ozone again becomes higher than the rate of Am(VI) reduction to Am(V) :



Hydrogen peroxide, H_2O_2 , which is a product of radiolysis of aqueous solution under the action of ^{241}Am α -particles, can be possible reductant in reaction (1). H_2O_2 and hydroperoxy radical HO_2 can also arise from ozone decomposition by the scheme proposed in [4]:



To find the causes of reductant accumulation in the solution, we estimated the contribution of the radiation factor to the reaction studied. For this purpose, we repeated the above experiment with ^{243}Am , whose specific radioactivity is by a factor of 15 lower than that of ^{241}Am , and found that this substitution did not affect the process: the amplitude of Am(VI) con-

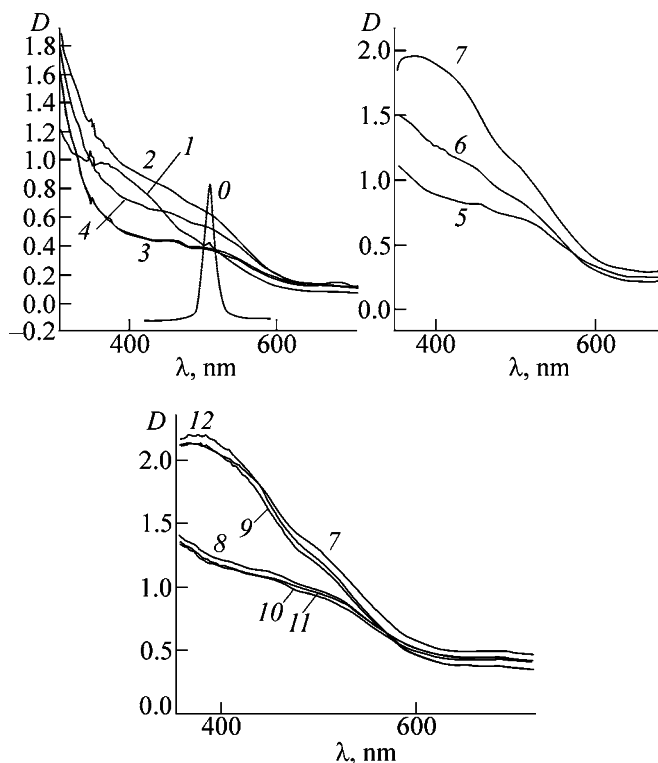


Fig. 1. Changes in absorption spectra of Am bicarbonate solutions during ozonation. O_3 content in the ozone–oxygen mixture 3.5%; 20°C; $l = 1$ cm. $[\text{NaHCO}_3]$ 0.12 M. (0) Spectrum of the initial Am(III) solution before Am(OH)_3 precipitation. Ozonation time, min: (1) 4, (2) 8, (3) 15, (4) 30, (5) 40, (6) 50, (7) 60, (8) 90, (9) 105, (10) 120, (11) 135, and (12) 165.

centration oscillations between upper and lower extremal points remained unchanged. As in the case of ^{241}Am , the oscillations were observed only at ozone bubbling through the solution, and when ozone bubbling was stopped, no changes in the reaction medium were observed. The maximal yields of both ^{241}Am and ^{243}Am in the hexavalent form were practically the same. Thus, the data obtained suggest that the main source of reductant in the system is the ozone decomposition followed by formation of hydroperoxy radicals and hydrogen peroxide, which reduce Am(VI) in the solution.

It should be noted that, in the above experiments, we used solutions with relatively low americium concentration, not exceeding 8×10^{-4} M. At ^{243}Am concentration $\leq 10^{-3}$ M, the pattern somewhat changes. In this case, after ^{243}Am oxidation to Am(VI) and start of the oscillatory process, a brown precipitate is formed in the system. Small portions of the precipitate were taken after stopping ozonation. It was soluble in 0.1 M NaHCO_3 and in 1 M HNO_3 . The spectra of

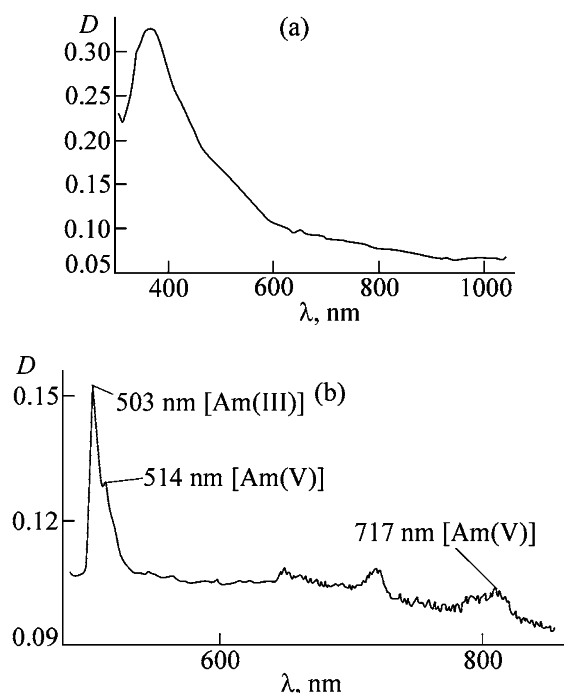


Fig. 2. Absorption spectra of the solutions obtained by dissolution of the precipitate formed during Am(OH)₃ ozonation in 0.1 M NaHCO₃ for 90 min (a) in 0.1 M NaHCO₃ and (b) in 1 M HNO₃.

these solutions are shown in Fig. 2. The spectrum in Fig. 2a is identical to the spectrum of Am(IV) carbonate complex described in [3]; no Am(III) was found in the solution.

In the spectrum of the precipitate in 1 M HNO₃, bands characteristic for hydrated Am³⁺ and AmO₂⁺ cations are observed (Fig. 2b). We can suggest that both Am(III) and Am(V) are formed by Am(IV) disproportionation in the stage of the precipitate dissolution in HNO₃. Am(IV), in turn, arises from Am(V) reduction with hydrogen peroxide formed by reactions (2)–(4), in accordance with the reactions [5]



Since the period of oscillations of Am(VI) concentrations in the solution was relatively short, only a part of Am(IV) precipitate formed had time to dissolve in the bicarbonate solution before formation of a new precipitate portion. As a result, a steady state was attained, and the americium distribution between the solution and precipitate remained virtually constant during the experiment (up to 1 h from the start of the oscillatory process). About 15% of Am from the total content of 1.3×10^{-3} M ²⁴³Am in the solution passed into the precipitate. Thus, as the initial Am content in the bicarbonate solution to be ozonized is increased, the Am(VI) yield, under equal other conditions, decreases.

From the data obtained, we can conclude that the method of Am(VI) preparation by ozonation of Am(III) hydroxide suspension in bicarbonate solutions is a complex multistep process, transforming with time into oscillatory mode, in which the Am(VI) yield depends of the initial americium content. Therefore, to obtain pure Am(VI) solution, continuous spectrophotometric monitoring of the Am valence forms in the solution is required.

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