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Photochemical Production of Tetravalent Americium in Hydrogencarbonate–Carbonate Media

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A new method of Am^{IV} production in hydrogencarbonate–carbonate media at pH 8.3–10.5 by UV-irradiation of americium(III) solutions containing $S_2O_8^{2-}$, BrO_3^- or BrO^- ions, or saturated with N_2O, is suggested.

Production of transplutonium elements (TPE) with oxidation states greater than 3 has been always an interesting problem both for general scientific interest and for the development of methods of actinide separation. For TPE the trivalent state in aqueous solution is most stable, but for americium oxidation states +4, +5, +6 and +7 are also known. Pulse radiolysis studies show that Am^{IV} exists in acid solutions for less than a few ms.[1,2] This oxidation state of americium is stabilized in the presence of ligands, forming stable complexes, *e.g.* in hydrogencarbonate–carbonate solutions.[3] The main way to obtain Am^{IV} is by electrochemical oxidation of Am^{III},[3–6] while under chemical oxidation Am^{V} and Am^{VI} usually form. There is to date only one reference relating to chemical methods of obtaining Am^{IV} in such media: *via* oxidation of Am^{III} by persulfate ions in the presence of Ag^+.[7]

In the present report a new effective way of obtaining Am^{IV} in hydrogencarbonate–carbonate solutions is suggested. This involves photochemical oxidation of Am^{III}, allowing a wide range of oxidants to be used, and even using carbonate ions for this aim.

Work was carried out using the ^{243}Am isotope with the small admixture of ^{241}Am and ^{244}Cm (α-activity 2.6% and 2.4% respectively). Potassium and sodium carbonates and hydrogencarbonates were of reagent grade not less than analytical purity. Aliquots of the initial 10^{-2} mol

$dm^{-3}Am(ClO_4)_3$ solution were added to a hydrogencarbonate–carbonate solution of the stated concentration at a known pH value. We soon noted that small quantities of ClO_4^- ions did not influence the experimental results. After the injection of oxidant and final pH measurements the solution was placed into a quartz spectrophotometric cell and was irradiated by UV light (two Hg-lamps of 120 W power with a quartz focusing lens).

Identification of the americium valency forms and the determination of Am^{IV} concentration was performed spectrophotometically and titrimetrically.[4,6] The maximum absorption band of Am^{IV} is at 369 nm. We determined a value of molar absorptivity for Am^{IV} $\varepsilon_{369} = 3150$ dm^3 mol^{-1} cm^{-1}; this is *ca.* 10% higher than the literature data.[4] The reason for this disagreement is possibly the incomplete oxidation of Am^{III} in ref. 4. Titrimetry was performed on solutions of H_2O_2 and $K_4Fe(CN)_6$; in hydrogencarbonate–carbonate solutions both reagents reduce Am^{IV} to Am^{III}, and Am^{VI} to Am^V. The presence of the ion-oxidants studied does not influence this fact.

It was found that in 1–3 mol dm^{-3} hydrogencarbonate–carbonate solutions americum ions show some photochemical activity. Under irradiation of $(1–3) \times 10^{-4}$ mol dm^{-3} Am^{III} solutions at pH 9.5-10.5, slow accumulation of Am^{IV} proceeds (during some hours) though it is impossible to obtain Am^{IV} quantitatively. Under the irradiation of Am^V, the formation of Am^{IV} also takes place, but simultaneously a small quantity of Am^{VI} seems to form ($\sim$15% in ratio to Am^{IV}). After 1–2 h of irradiation the system came to equilibrium containing Am^{IV}, Am^V and Am^{VI}. This state was maintained at further irradiation for several hours. In the mixture of Am^{III} with Am^V the formation of Am^{IV} is faster, and Am^{III}, Am^{IV} and Am^V are in equilibrium already. Consequently, in americium hydrogencarbonate–carbonate solutions photochemical reactions proceed with the participation of molecules and ions of the medium. However, their efficiency is low. The obtention of Am^{IV} is much more effective in the presence of oxidants.

We studied the possibility of photochemical oxidation of Am^{III} in hydrogencarbonate–carbonate solutions, containing oxidant ions $S_2O_8^{2-}$, BrO^-, BrO_3^-, ClO_3^- and IO_3^-, and also in solutions without oxidants, saturated with N_2O. In all these systems photochemical oxidation of Am^{III} is observed. Without UV irradiation Am^{III} is not in practice oxidized (with the exception of solutions with $S_2O_8^{2-}$, but this case can be ignored by comparison with photochemical processes). The ions ClO_3^- and IO_3^- are not capable of quantitative oxidation and we shall not discuss them further.

In solutions with $[CO_3^{2-}]+[HCO_3^-] >$ mol dm^{-3} and with pH 8.3–10.5 the photochemical method allows the quantitative oxidation of Am^{III} to Am^{IV}. The highest oxidation rate was achieved with $S_2O_8^{2-}$ ions, the lowest one in the system, saturated with N_2O. Oxidation proceeds according to a zero-order rate law. Thus, the radicals which form during photochemical decomposition of the initial ions are the oxidants in all cases. In the system saturated with N_2O these are the CO_3^- radicals, appearing during the photolysis of the carbonate solution. Because of the weak light absorbency of the CO_3^{2-} ions in the spectral region >250 nm (light with such a wavelength was used for photolysis) this process proceeds rather slowly, explaining the low accumulation rate of Am^{IV}: tens of minutes up to a concentration in the region of $1–2 \times 10^{-4}$ mol dm^{-3}. The process of oxidation by persulfate ions allows us to obtain *ca.* 10^{-3} mol dm^{-3} of Am^{IV} during several minutes. Fig.1 shows kinetic curves during the photochemical formation of Am^{IV} in systems with $S_2O_8^{2-}$, BrO^- and BrO_3^- ions under conditions for which the oxidation rate of Am^{III} does not already depend on the concentration of oxidant. Fig. 1 also shows the Am^{IV} accumulation kinetics in hydrogencarbonate–carbonate solution, saturated with N_2O. On decreasing the concentration of the stated ions, the oxidation rate of Am^{III} falls; on a logarithmic scale the slope of these dependences are: for $S_2O_8^{2-}$, 0.8; for BrO^-, 1.0; and for BrO_3^-, 0.5.

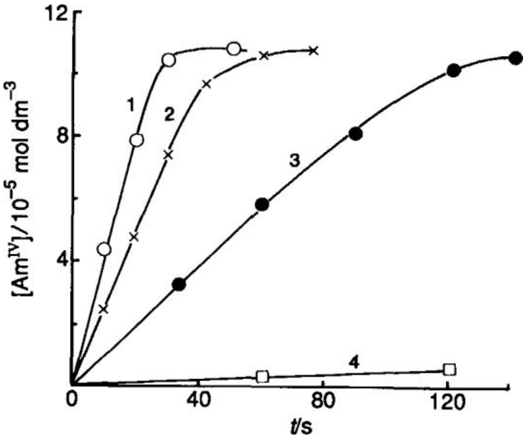

Fig. 1 Kinetics for Am^{III} photochemical oxidation in 1.5 mol dm^{-3} solution of $Na_2CO_3 + NaHCO_4$ at pH 9.88 under irradiation by the light flow of an Hg lamp; 1, by $S_2O_8^{2-}$ ions, 0.5 mol dm^{-3}; 2, by BrO^- ions, 0.013 mol dm^{-3}; 3, by BrO_3^-, 0.5 mol dm^{-3}; 4, in solution, saturated with N_2O, $[Am^{III}]_{init} = 1.1 \times 10^{-4}$ mol dm^{-3}.

As a rule the oxidation rate of Am^{III} to Am^{IV} becomes slower with increasing pH and $[CO_3^{2-}]+[HCO_3^-]$. This fact seems to be connected with the change in photochemical yield of the active particles or with the change in composition of Am^{III} carbonate complexes.

The photooxidation chemistry of Am^{III} in hydrogencarbonate–carbonate solutions is described by reactions (1)–(6) below. In the presence of N_2O the initial stage is the following, reaction (1).

$$CO_3^{2-} \xrightarrow{h\nu} CO_3^- + e_{aq}^- \qquad (1)$$

After this the following processes take place:[8]

$$N_2O + e_{aq}^- \longrightarrow N_2 + O^- \qquad (2)$$

$$O^- + H_2O \rightleftharpoons OH + OH^- \qquad (3)$$

$$CO_3^{2-} + OH \longrightarrow CO_3^- + OH^- \qquad (4)$$

$$HCO_3^- + OH \longrightarrow CO_3^- + H_2O \qquad (5)$$

$$Am^{III} + CO_3^- \longrightarrow Am^{IV} + CO_3^{2-} \qquad (6)$$

On ceasing irradiation and bubbling N_2O through, gaseous products evaporate from the hydrogencarbonate–carbonate solution of Am^{IV}, and the desired ion is obtained without admixtures of different ions.

In the system containing persulfate ions the following process [reaction (7)] is the main source of radical oxidisers:

$$S_2O_8^{2-} \xrightarrow{h\nu} 2SO_4^- \qquad (7)$$

It is possible that the subsequent stage is reaction (8),

$$SO_4^- + CO_3^{2-} \longrightarrow SO_4^{2-} + CO_3^- \qquad (8),$$

after which Am^{III} is oxidized according to reaction (6). The oxidation of Am^{III} by SO_4^- radicals cannot be ignored. Similar processes seem to take place in the presence of BrO_3^- and BrO^- ions; for example, reactions (9)–(13) below.

$$BrO^- \xrightarrow{h\nu} Br + O^- \qquad (9)$$

$$\mathrm{Br} + \mathrm{Br}^- \longrightarrow \mathrm{Br}_2^- \qquad (10)$$

$$\mathrm{Br}_2^- + \mathrm{CO}_3^{2-} \rightleftharpoons 2\mathrm{Br}^- + \mathrm{CO}_3^- \qquad (11)$$

$$\mathrm{Am}^{\mathrm{III}} + \mathrm{CO}_3^- \longrightarrow \mathrm{Am}^{\mathrm{IV}} + \mathrm{CO}_3^{2-} \qquad (12)$$

$$\mathrm{Am}^{\mathrm{III}} + \mathrm{Br}_2^- \longrightarrow \mathrm{Am}^{\mathrm{IV}} + 2\mathrm{Br}^- \qquad (13)$$

The quantum yield η for the oxidation of $\mathrm{Am}^{\mathrm{III}}$ to $\mathrm{Am}^{\mathrm{IV}}$ when irradiated by light λ 254 nm was measured by the method of ferrioxalate actinometry.[9] For solutions with pH 9.60–9.88 and $[\mathrm{CO}_3^{2-}]+[\mathrm{HCO}_3^-]=1.5$–$1.6$ mol dm^{-3}, η was the following: with $\mathrm{S}_2\mathrm{O}_8^{2-}$, 1.07 ± 0.13; with BrO^-, 0.56 ± 0.07; with BrO_3^-, 0.20 ± 0.03.

In the systems KHCO_3–$\mathrm{K}_2\mathrm{CO}_3$ and NaHCO_3–$\mathrm{Na}_2\mathrm{CO}_3$ the oxidation profiles of americium are practically the same.

It should be noted that $\mathrm{Am}^{\mathrm{III}}$ oxidizes to $\mathrm{Am}^{\mathrm{IV}}$ only when $[\mathrm{HCO}_3^-]+[\mathrm{CO}_3^{2-}]$ is $>$ 1 mol dm^{-3} and $8.3 < \mathrm{pH} < 10.5$. In 1–2 mol dm^{-3} $\mathrm{Na}_2\mathrm{CO}_3$ or 1–3 mol dm^{-3} $\mathrm{K}_2\mathrm{CO}_3$ ($\mathrm{pH} > 11$) in all cases the formation of $\mathrm{Am}^{\mathrm{VI}}$ took place. If $[\mathrm{CO}_3^{2-}]$ is increased to 4 mol dm^{-3} and more (it is possible in a solution of $\mathrm{K}_2\mathrm{CO}_3$), $\mathrm{Am}^{\mathrm{IV}}$ again becomes the final product of photochemical oxidation. Analogous regularities of the results of $\mathrm{Am}^{\mathrm{III}}$ oxidation were observed in electrochemical experiments.[5,7]

In this communication we report a new method of $\mathrm{Am}^{\mathrm{IV}}$ production in hydrogencarbonate–carbonate solutions which allows us to use different oxidizers, achieving a high oxidation rate, and also to perform the process without the addition other ions to the solution.

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