Preparation of Am^{IV} and Am^{VI} in bicarbonate and carbonate solutions using xenon compounds

A. B. Yusov, A. V. Anan'ev, and V. P. Shilov*

Institute of Physical Chemistry, Russian Academy of Sciences,
31 Leninsky prosp., 117915 Moscow, Russian Federation.
Fax: +7 (095) 335 1778

Xe compounds, XeF_2, Na_4XeO_6, and XeO_3, were used to oxidize Am^{III} in carbonate and bicarbonate aqueous solutions. XeF_2 and XeO_3 may be used to obtain Am^{IV} in solutions, whereas Na_4XeO_6 oxidizes Am^{III} into Am^{IV}+Am^{V}+Am^{VI} or into Am^{VI} if present in excess. XeO_3 reacts with Am^{III} to give Am^{IV} only under UV irradiation.

Key words: americium(III); americium(IV); xenon difluoride, sodium perxenate, xenon trioxide as oxidants.

The preparation of higher valent states of transplutonium elements in solutions is an important problem. It is known that Am^{V} and Am^{VI} compounds are formed rather easily; Am^{IV} is much more difficult to obtain, requiring the use of strongly complex-forming media, *e.g.*, carbonate solutions. However, the first attempts to oxidize Am^{III} in carbonate solutions with ozone or persulfate[1,2] afforded only Am^{V} and Am^{VI}. Only in the beginning of 80's the conditions for the formation of Am^{IV} by the electrochemical oxidation of Am^{III} in carbonate solutions were found. It was shown that Am^{IV} is stable at pH 8.4–10.0 (see Ref. 3). Later, a chemical oxidant was found (a Ag^+—$S_2O_8^{2-}$ system).[4] This chemical method of the formation of Am^{IV} in carbonate solutions, unique up to recent times, has an evident drawback, *viz.*, the contamination of the solution with Ag ions. In our previous work,[5] a photochemical method for forming of Am^{IV}, devoid of this drawback, was proposed.

In the following investigations we tested xenon compounds as oxidants. The oxidation potentials (E) of some Xe compounds exceed those of the Am^{IV}/Am^{III} pair in carbonate solutions ($E = 0.99 \div 0.81$ V depending on pH (8.9—11.2)).[6] For example, in alkaline media $E_{HXeO_4^-/Xe} = 1.24$ V (*cf.* Ref. 7) and $E_{HXeO_6^{3-}/XeO_4^-} \approx 0.9$ V (*cf.* Ref. 8), and the potentials increase when pH decreases. The potential of the XeF_2/Xe pair has been estimated only in acidic media: $E_{XeF_2/Xe} = 2.3$ V (*cf.* Ref. 7). These data show that xenon compounds can oxidize Am^{III} in carbonate solutions.

The addition of XeF_2 to a $(1—4) \cdot 10^{-4}$ *M* solution of Am^{III} in a 1.5 *M* aqueous solution of $KHCO_3$ or 1.5 *M* solution of ($KHCO_3$ + K_2CO_3) turns the colorless reaction mixture yellow. In the UV absorption spectrum the intensity of the Am^{III} band at 507—508 nm is decreased and a band with a maximum at 360—370 nm is observed. The shape of the profile attests to the four-valent state of americium. This fact is confirmed by titration with a $K_4Fe(CN)_6$ solution, which results in a decrease in the intensity of the band at 370 nm and an increase in the absorption at 507—508 nm. In a 1.5 *M* aqueous solution of K_2CO_3 without the addition of $KHCO_3$ the oxidation of americium becomes less effective, and increasing the K_2CO_3 concentration to 3—5.9 mol L^{-1} stops altogether.

Sodium perxenate, Na_4XeO_6, also oxidizes Am^{III} in aqueous $KHCO_3$ and ($KHCO_3$ + K_2CO_3) solutions, but the oxidation proceeds in another way. If for example solid Na_4XeO_6 or its freshly prepared solution is added to a $(1—2) \cdot 10^{-4}$ *M* solution of Am^{III} up to $1 \cdot 10^{-4}$ mol L^{-1} concentration, the absorption in the range of $\lambda < 600$ nm with the maximum at ~360—370 nm increases after *ca.* 1 min. However, the comparison of intensities of the bands at 370 nm, where Am^{IV} and Am^{VI} have almost equal extinction, and at 600 nm, where the extinction of Am^{VI} exceeds that of Am^{IV} threefold, shows that Am^{IV} and Am^{VI} are accumulated in the solution. However, their sum is less than the decrease in the amount of Am^{III}, and, hence, Am^{V}, which has no characteristic absorption bands, is also present in solution. When the concentration of Na_4XeO_6 is increased to $3 \cdot 10^{-3}$ mol L^{-1}, Am^{III} converts completely into Am^{VI}. In a 5.9 *M* solution of K_2CO_3, the perxenate anion decomposes, but Am^{III} does not undergo oxidation.

Xenon trioxide, XeO_3, is practically inert with respect to Am^{III} in aqueous solutions of $KHCO_3$, ($KHCO_3$ + K_2CO_3), and K_2CO_3. UV irradiation with a SVD-120A mercury lamp or a DKsSh-500 xenon lamp was used for its activation. Under UV irradiation in a 1.5 *M* aqueous solution of ($KHCO_3$ + K_2CO_3) in the presence of XeO_3 ($5 \cdot 10^{-5}$—$2 \cdot 10^{-3}$ mol L^{-1}), Am^{III} is converted into Am^{IV}, which is confirmed by changes in the absorption spectrum and by titration with a

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 953—954, May, 1994.

1066-5285/94/4305-0899 $12.50

$K_4Fe(CN)_6$ solution: after the titration, americium returns to the initial three-valent state. The rate of oxidation increases with the increase in XeO_3 concentration and depends only slightly on the composition of the solution. In 1.5–3 *M* solutions of K_2CO_3 containing XeO_3 the photochemical oxidation of Am^{III} to Am^{VI} takes place.

Thus, xenon compounds are useful for oxidation of Am^{III} in carbonate solutions. A new reagent, XeF_2, useful for preparation of Am^{IV} by chemical methods in bicarbonate—carbonate solutions has been found; the oxidant is decomposed completely, and the small amount of F^- that is introduced into the solution, has no significant effect on the behavior of Am^{IV}. The presence of F^- ions in the solution can be avoided if XeO_3 is used, but the formation of Am^{IV} in that case proceeds only under UV irradiation. To obtain Am^{VI}, Na_4XeO_6 may be used, but a large excess of oxidant must be taken.

The present work was supported by the Russian Foundation for Basic Research (Project 93—03—4510).

Experimental

The quality of the reagents used, the procedures for the preparation of purified Am samples and carbonate solutions of americium, and the description of the spectrophotometrical investigations have been given elsewhere.[5,9] The procedure for the titration of Am^{IV} and Am^{VI} solutions has been described previously.[3] XeF_2 and Na_4XeO_6 were used without additional purification and were introduced into solutions in the crystalline state or in the form of a solution in ice-cold water. XeO_3 was obtained by hydrolysis of Na_4XeO_6 in a 0.1 *M* $HClO_4$ solution.

References

1. J. S. Coleman, T. K. Keenan, and L. H. Jones, *Inorg. Chem.*, 1963, **2**, 58.
2. V. A. Ermakov, A. G. Rykov, G. A. Timofeev, A. V. Dzhzadav, and G. N. Yakovlev, *Radiokhimiya*, 1973, **15**, 380 [*Sov. Radiochem.*, 1973, **15** (Engl. Transl.)].
3. D. E. Hobart, K. Samhoun, and J. R. Peterson, *Radiochim. Acta*, 1982, **31**, 139.
4. P. L. Khizhnyak, Ph. D. Thesis., Moscow, 1987 (in Russian).
5. A. B. Yusov and V. P. Shilov, *Mendeleev Commun.*, 1993, 83.
6. P. Berger, P. Blank, and J. Bourges, *Radiochim. Acta*, 1988, **43**, 217.
7. V. D. Klimov, V. N. Prusakov, and V. B. Sokolov, *Radiokhimiya*, 1971, **13**, 725 [*Sov. Radiochem.*, 1971, **13** (Engl. Transl.)].
8. E. H. Appelman and J. G. Malm, *J. Am. Chem. Soc.*, 1964, **86**, 2141.
9. V. P. Shilov and A. B. Yusov, *Radiokhimiya*, 1971, **13**, 725 [*Sov. Radiochem.*, 1971, **13** (Engl. Transl.)].

Received December 30, 1993;
in revised form February 8, 1994

Nucleophilic substitution of bromine in vicinal bromotrifluoroalkylamines

Yu. L. Ignatova,* N. M. Karimova, and I. N. Rozhkov[†]

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: + 7 (095) 135 5085

Secondary *N*-(2-bromo-3,3,3-trifluoropropyl)-*N*-alkylamines cyclize under the action of bases to yield aziridines. Tertiary *N*-(2-bromo-3,3,3-trifluoropropyl)amines react with S-nucleophiles to give products of bromine substitution.

Key words: *N*-(2-bromo-3,3,3-trifluoropropyl)-*N*-alkylamines, nucleophilic substitution; 2-trifluoromethylaziridines.

Compounds containing the CF_3 group are of significant interest as potentially biologically active substances. However, the methods for the synthesis of these compounds are rather limited, because the nucleophilic substitution in trifluoromethylated alkyl halides is hindered.[1–3] The rate of nucleophilic substitution of the halogen in α-fluorinated ethyl halides is several orders

---

[†] Deceased in 1993.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 5, pp. 955—957, May, 1994.

1066-5285/94/4305-0900 $12.50