Chemical Effects Associated with β-Decay Process. I. The Chemical Behavior of a Decayed Product, ^{144}Pr, in the EDTA Complex System

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Many papers on the chemical effects of β-decay processes have appeared in current literature, with especial emphasis laid on the change in the oxidation state of radioactive daughter atoms. It has been widely accepted that the unusual behavior of radioactive daughter atoms is to be attributed, in the main, to an electronic excitation resulting from the abrupt change in the nuclear charge. On the other hand, the probability of a bond rupture resulting from the recoil only is fairly small, because in many cases the effective recoil energy and the chemical bond energy are of the same order of magnitude.

The lanthanides provide an opportunity to study the chemical behavior of the radioactive daughter atoms formed by the β-decay process, especially the effects of the electronic excitation; that is, their chemical properties are similar to each other, and the daughter atoms are in an excited state or are thermodynamically unstable, even in the simple β-decay.

Cerium-praseodymium-144 possesses several advantages in its nuclear and chemical properties for this purpose. The present investigation will study the chemical behavior of ^{144}Pr atoms formed by the β^--decay of the ^{144}Ce-labeled cerium(III) ethylenediaminetetraacetate (Ce(III)-EDTA) complex in aqueous and aqueous-alcohol solutions. Previously, the chemical behavior of ^{144}Pr in the ^{144}Ce(III) acetylacetonate system was investigated by Edwards and Coryell(1) and was found to be considerably different from that of the parent ^{144}Ce. In the lanthanide system it was also reported that 59 per cent of the ^{177}Lu atoms formed by the

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1) R. R. Edwards and C. D. Coryell, TID-13363 (1961).

β^--decay of the ^{177}Yb(III)-EDTA complex escape from the complex, and appear in solution in the cationic form, $^{177}Lu^{3+}$.[2]

Experimental

Reagents.—Carrier-free Ce-Pr-144 in a hydrochloric acid solution was imported from the Oak Ridge National Laboratory. The solution of disodium ethylenediaminetetraacetate (EDTA) was standardized against a standard zinc(II) solution by volumetric titration, using Eriochrome Black T as an indicator. A stock solution of cerium(III) was prepared by dissolving guaranteed-reagent-grade $Ce(NO_3)_3 \cdot 6H_2O$ in hydrochloric acid, and it was standardized volumetrically against the standard EDTA solution with Eriochrome Black T. All the other chemicals used were of guaranteed-reagent grade.

Apparatus and Procedure.—An aliquot of the cerium(III) chloride solution labeled with ^{144}Ce was evaporated to dryness in the presence of hydrogen peroxide. To the solid cerium(III) chloride, a known amount of a EDTA solution was added, less in amount than the equivalent ([EDTA]/[Ce(III)] = 0.766), and then the Ce(III)-EDTA complex solution was prepared by passing it through a Dowex 50W-X8 column at pH 6.5 in order to remove the excess cerium. The separate experiments ensured that the separation was quantitative, indicating the presence of no excess EDTA. The final concentration of cerium(III) was 1.2×10^{-3} M. The pH was adjusted by the addition of an ammonium acetate buffer. Aliquots of the solution were allowed to stand in a bath of the desired temperature for 4 hr. The samples were then withdrawn through a Dowex 50W-X8 column (8 mm. × 20 mm.), and the free-ion fraction was separated from the complex fraction. The resin used had been treated previously with an appropriate buffer.

The yield of the free-ion fraction was obtained by counting the γ-activities of both the resin phase and the combined effluents. The cerium-144 was assayed by counting only the hard γ-activities of ^{144}Pr in secular equilibrium with ^{144}Ce 3 hr. later. The yield of ^{144}Pr ions was obtained by extrapolating the ^{144}Pr decay (or growth) curve to the time of chemical separation, using the half-life of 17.5 min.[3] The pH of the solution was measured with a glass-electrode pH meter, with an accuracy of 0.02 pH.

Results

The experiments have shown that the apparent yield of the ^{144}Pr ion, which is defined as the extent of the free-ion fraction absorbed on the resin, depends on the pH, the concentration of ethyl alcohol, and the temperature.

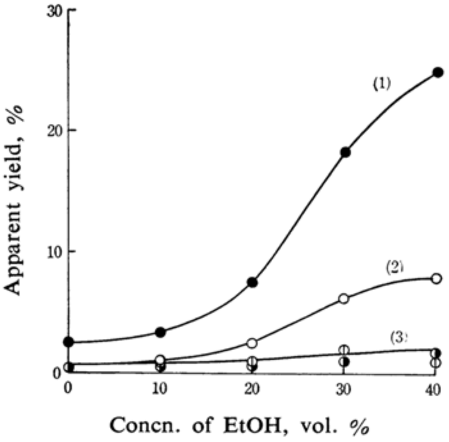

Fig. 1. Effect of concentration of ethyl alcohol on apparent yields of $^{144}Pr^{3+}$ and $^{144}Ce^{3+}$ at pH 6.7.
(1) and (2) : ^{144}Pr ; (3) : ^{144}Ce
○ and ⦶ : 28°C ; ● and ◑ : 3°C

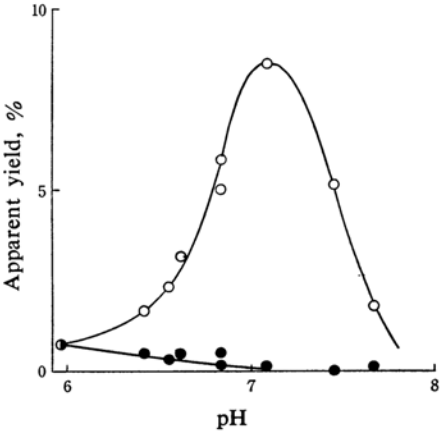

Fig. 2. Apparent yields of $^{144}Pr^{3+}$ and $^{144}Ce^{3+}$ in aqueous solution at 3°C.
○ : ^{144}Pr ; ● : ^{144}Ce

As Fig. 1 shows, the apparent yield of ^{144}Pr ions increases slightly up to 20 per cent ethyl alcohol, while above this point the yield increases abruptly. The maximum concentration of ethyl alcohol used in the experiments was 40 per cent because of the small solubility of the Ce(III)-EDTA complex.

The distribution of the apparent yields of ^{144}Pr ion and ^{144}Ce ion as a function of the pH at a constant temperature is shown in Figs. 2 and 3. These figures show that there is a remarkable difference between the distribution curves of ^{144}Pr and ^{144}Ce. For instance, the yield of free cerium ions decreases gradually as the pH increases, whereas the distribution curves of praseodymium have a maximum.

According to the formation constant of the

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[2] P. Glentworth and R. H. Betts, *Can. J. Chem.*, **39**, 1049 (1961).

[3] B. S. Dzhelepov and L. K. Peker, "Decay Schemes Radioactive Nuclei," Pergamon Press, New York (1961), p. 422.

Ce(III)-EDTA complex,[4] cerium(III) forms completely the complex with EDTA under these experimental conditions. Because of the absence of excess EDTA, however, it should be noted that the cerium absorbs to some extent on the resin as the apparent formation constant decreases. These facts are clearly shown by the distribution behavior of ^{144}Ce in Figs. 2 and 3.

The distribution curves of ^{144}Pr may be influenced by both the normal distribution and the so-called "hot-atom" effect. To obtain the net "hot-atom" effect of ^{144}Pr, we subtracted the extent of normal distribution from the apparent distribution curve, on the assumptions that the normal distribution curve of praseodymium is similar to that of cerium, and that the distribution constants of cerium and praseodymium are equal. The results are shown in Fig. 4.

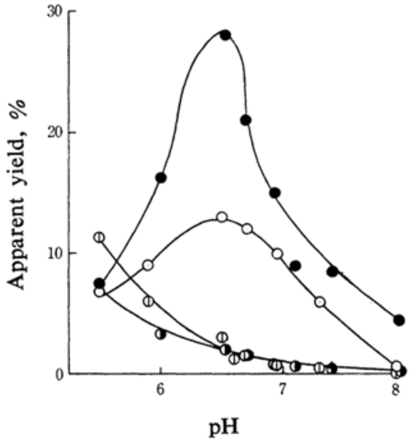

Fig. 3. Apparent yields of ^{144}Pr^{3+} and ^{144}Ce^{3+} in 40 % alcohol solution.
○ and ●: ^{144}Pr; ⦶ and ◑: ^{144}Ce
○ and ⦶: 25°C; ● and ◑: 3°C

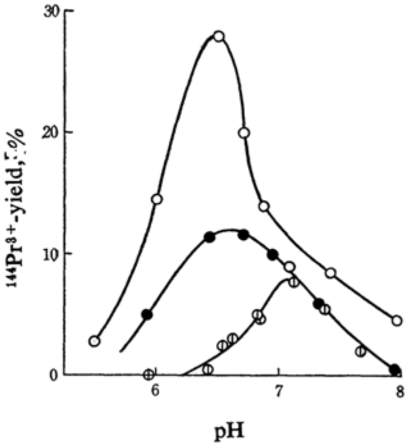

Fig. 4. ^{144}Pr^{3+}-yield as a function of pH.
⦶: Aqueous solution at 3°C
●: 40 % alcohol solution at 25°C
○: 40 % alcohol solution at 3°C

Discussion

The maximum yield of the ^{144}Pr ion is 28 per cent in a 40 per cent alcohol solution at 3°C, suggesting that in at least 28 per cent of the events the cerium(III)-EDTA bonds were ruptured as a result of the β^--decay of ^{144}Ce. Since the nuclear event itself is insensitive to the surrounding conditions, the extent of the bond rupture should also be independent of the pH. The results shown in Fig. 4, therefore, suggest that, after nuclear events, the deexcited ^{144}Pr atom causes a chemical reaction with environmental substances during its lifetime.

It has been found that the rate of isotopic exchange reaction in the La(III)(Nd(III))-EDTA systems is fairly rapid.[5] In these systems, the rate of the exchange reaction, R, is expressed as:

$$R=k[\mathrm{LnY}^-]\ [\mathrm{H}^+] \qquad (1)$$

where k is a rate constant of about 10^5 l.·mol^{-1}min^{-1} and where LnY$^-$ designates the EDTA complex. Although the mechanism of the exchange reaction in the alkaline region has not been investigated, the mechanism seems to be similar to that in the In(III)-EDTA system:[6]

$$R=k[\mathrm{InY}^-]\ [\mathrm{OH}^-]^2 \qquad (2)$$

in which the rate of exchange is expressed as in Eq. 1 in the acid region. These values of the rate constants cannot be directly applied to the present system. On the basis of kinetics, however, the distribution curves of ^{144}Pr ion can be qualitatively explained. In the neutral region, the exchange rate has a minimum value, producing a maximum point in the distribution curve. The pH at which the yield of ^{144}Pr ions is at a maximum shifts to a lower value with an increase in the concentration of ethyl alcohol. These results suggest that the reaction expressed in Eq. 1 is depressed as compared with the reaction expressed in Eq. 2 in the alcoholic solution. As the temperature rises, the re-chelation of ^{144}Pr with EDTA

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[4] J. Bjerrum, G. Schwarzenbach and L. G. Sillén, "Stability Constants of Metal Ion Complexes, Part I. Organic Ligands," The Chemical Society, London (1958), p. 76.

[5] R. H. Betts, O. F. Dahlinger and D. M. Munro, "Radioisotopes in Scientific Research. Proceedings of the First UNESCO International Conference, Paris, 1957," Vol. II, Pergamon Press, New York (1958), p. 326.

[6] K. Saito and M. Tuchimoto, *J. Inorg. Nucl. Chem.*, 25, 1245 (1963).

will be promoted; therefore, the yield of ^{144}Pr ion decreases with the temperature. These considerations lead to the conclusion that, in the ^{144}Ce(^{144}Pr)-EDTA system, the very extensive disruption of the EDTA complex takes place as a result of the β^--decay of ^{144}Ce.

The cerium-144 is transformed to ^{144}Pr by β^--decay with energies of 0.320 (60 per cent) and 0.184 (30 per cent) MeV.[3] The recoil energy is low, ranging from 0 to 1.6 eV. according to the partition of energy between the β^--particle and neutrino. This means that the probability of bond rupture as a result of the recoil only is much less than 1. Consequently, the fairly complete disruption of the complex may arise from the abrupt change in the atomic number of the metal ion.

Positively-charged species result from the increase in the nuclear charge in the β^--decay, even in the absence of orbital electron ionization. At the instant of the simple β^--decay of the ^{144}Ce(III)-EDTA complex, ^{144}Pr exists in the tetravalent state, and the instability of tetravalent praseodymium in solution is favorable for an instantaneous stabilization reaction. For this stabilization reaction, it was suggested that, in the β^--decay of ^{144}Ce(III) acetylacetonate, the electron transfer of tetravalent ^{144}Pr with parent cerium(III) acetylacetonate might reduce the excited complex to stable ^{144}Pr(III) acetylacetonate.[1] In the present system, however, considering that the EDTA is a reducing agent,[7] it is most probable that the electron transfer between the tetravalent ^{144}Pr and EDTA is predominant and that it, via an intermediate complex, results in the extensive bond rupture needed to liberate the ^{144}Pr ion. Moreover, it has been confirmed that such an intramolecular electron-transfer is often followed by a bond-rupture process.[8] (In order to treat the results strictly, however, it should be borne in mind that the presence of higher-charged ^{144}Pr in consequence of internal conversion cannot be ignored.)

Although the explanation offered here is not rigorous, it will be recognized that the most important factor in determining the fate of ^{144}Pr atoms is an increase in the nuclear charge of ^{144}Pr as a result of the β^--decay of ^{144}Ce. Furthermore, it is evident that the exchange reaction plays an important part in determining the ^{144}Pr^{3+}-yield, even if the question remains unresolved of whether the intermediate complex has a finite lifetime, or whether it decomposes instantaneously.

Summary

The chemical behavior of ^{144}Pr formed by the β^--decay of the ^{144}Ce(III)-EDTA complex has been investigated. The chemical behavior of ^{144}Pr is remarkably different from that of ^{144}Ce. The results suggest that an increase in the nuclear charge of ^{144}Pr plays the most important role in determining the yield of ^{144}Pr ions and leads to the extensive disruption of the complex molecule by intramolecular electron-transfer. The liberated ^{144}Pr ion reforms the complex according to its kinetic law. The recoil as a result of β^--decay seems not to be the cause of the formation of the free ^{144}Pr ions.

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[7] T. Moeller, F. A. J. Moss and R. H. Marshall, *J. Am. Chem. Soc.*, 77, 3182 (1955).

[8] D. R. Stranks, "Modern Coordination Chemistry," Ed. by J. Lewis and R. G. Wilkins, Interscience Pub. Inc., New York (1960), p. 160.