Chemical Effects Associated with the β-Decay Process. II. A Kinetic Study of the Chemical Behavior of ^{144}Pr in the EDTA Complex System

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Unusual chemical behavior of a radioactive daughter atom may result from an increase in the nuclear charge produced by β^--decay.[1] The effects of the increase include such secondary processes as an electronic excitation due to a sudden change in the nuclear charge, and rotational and vibrational excitations due to recoil. It is very difficult to evaluate the effects associated with β^--decay in the liquid system, in contrast to those taking place in the gas phase. In the Ce-Pr-144 system, however, the probability of a bond-rupture arising from the recoil by β^--decay is expected to be much smaller, since the maximum recoil energy imparted to a free, isolated ^{144}Pr atom is only 1.6 eV. It was also suggested in the preceding paper[2] that the thermodynamical instability of a ^{144}Pr atom plays an important role in determining its chemical behavior. Accordingly, the experimental results could be explained qualitatively by a mechanism which includes the decomposition of an intermediate complex produced by intramolecular electron-transfer, in addition to the substitution reaction between the liberated ^{144}Pr ion and the cerium(III) ethylenediaminetetraacetate (Ce(III)-EDTA) complex.

More experimental evidence is needed to substantiate this model. The present authors have, therefore, attempted to elucidate quantitatively the chemical behavior of ^{144}Pr atoms in terms of the per cent yield of the ^{144}Pr(III)-EDTA complex (the ^{144}PrY$^-$-yield). Moreover, in order to study the kinetics of the ^{144}PrY$^-$-yield, the substitution reactions of the cerium(III) ion and the Pr(III)-EDTA complex were investigated in an aqueous solution using ^{144}Ce as a tracer.

Experimental

The chemicals employed were the same as those described previously.[2]

The kinetic runs were carried out as follows: an aqueous solution of the Pr(III)-EDTA complex was mixed with praseodymium(III) chloride containing ^{144}Ce at 25±0.1°C. The ionic strength was adjusted using 0.50 M sodium chloride, and then 0.04 M sodium acetate was added as a buffer. As will be mentioned later, the exchange rate is affected by the presence of acetate ions, so the total concentration of acetate ions was maintained at 0.04 M in order to minimize such effect. At suitable times, samples were withdrawn rapidly through a Dowex 50W-X8 column (0.5 g. of resin) which had been previously treated with an appropriate buffer. The column was then washed with a known amount of buffer, and the combined eluates (that is, the fraction containing the complex) were collected in a test tube. The separate experiments ensured that the free-ion fraction was separated quantitatively from the complex fraction.

The ^{144}PrY$^-$-yield, which was defined as the ratio of the γ-activity of the eluate to the total activity, was obtained similarly, after a complete equilibration with respect to ^{144}Ce had been attained chemically.

The γ-activity of each liquid sample was determined with a well-type scintillation spectrometer. The ^{144}Ce and ^{144}Pr were assayed by essentially the same methods as had been employed previously.[2] The pH of the solution at the equilibrium was measured by a glass-electrode pH meter, with an accuracy of 0.01 pH.

Results and Discussion

The Substitution Mechanism.—In the preliminary experiments on the isotopic exchange reaction of ^{144}Ce(III) ion and Ce(III)-EDTA complex, it was found that the rate of the exchange reaction, R, may be expressed as:

$$R=k_{\mathrm{Ce,\,app}}\,[\mathrm{CeY^-}]\,[\mathrm{H^+}] \qquad (1)$$

where $k_{\mathrm{Ce,\,app}}$ is the apparent rate constant, depending on the concentration of acetate ions, and Y^{4-} indicates a tetravalent EDTA anion. The main path leading to exchange is the acid-catalyzed dissociation of the Ce(III)-EDTA complex, which is in accordance with the mechanism suggested by Betts et al.[3]

The substitution reaction of the cerium(III)

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[1] S. Wexler, "Chemical Effects of Nuclear Transformations (Prague Conf.)," Vol. I, IAEA, Vienna (1961), p. 115.

[2] T. Shiokawa, H. Kudo and T. Omori, This Bulletin, 38, 1340 (1965).

[3] 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.

ion and the Pr(III)-EDTA complex may be expressed stoichiometrically as follows:

$$^{144}\mathrm{Ce}^{3+} + \mathrm{PrY}^- \rightleftarrows {}^{144}\mathrm{CeY}^- + \mathrm{Pr}^{3+} \qquad (2)$$

On the basis of the isotopic exchange reaction, the path of the substitution will be:

$$\mathrm{PrY}^- + \mathrm{H}^+ \xrightarrow{k_{\mathrm{Pr,\,app}}} \mathrm{Pr}^{3+} + \mathrm{HY}^{3-} \qquad (3)$$

followed by a very fast reaction:

$$\mathrm{Ce}^{3+} + \mathrm{HY}^{3-} \xrightarrow{k'_{\mathrm{Ce}}} \mathrm{CeY}^- + \mathrm{H}^+ \qquad (4)$$

The reverse reactions, whose rate constants are designated by k'_{Pr} for Eq. 3 and $k_{\mathrm{Ce,\,app}}$ for Eq. 4, would take place simultaneously. In these expressions, Pr^{3+} and Ce^{3+} represent the species in the cationic form, including acetate complexes. These, however, may be allowed, since the exchange rate is independent of the nature of the free metal ion. It is also permissible to set $k'_{\mathrm{Ce}} = k'_{\mathrm{Pr}}$. Hence, the overall rate equation is given by:

$$\frac{\mathrm{d}[\mathrm{CeY}^-]}{\mathrm{d}t} = k_{\mathrm{Pr,\,app}}[\mathrm{PrY}^-][\mathrm{H}^+]\frac{[\mathrm{Ce}^{3+}]}{[\mathrm{Ce}^{3+}]+[\mathrm{Pr}^{3+}]} - k_{\mathrm{Ce,\,app}}[\mathrm{CeY}^-][\mathrm{H}^+]\frac{[\mathrm{Pr}^{3+}]}{[\mathrm{Ce}^{3+}]+[\mathrm{Pr}^{3+}]} \qquad (5)$$

Since the kinetic measurements are carried out with solutions containing both the praseodymium(III) ion and the Pr(III)-EDTA complex in a large excess over carrier-free ^{144}Ce, the substitution reaction can be treated as a pseudo-first order reaction; the reaction rate may thus be simplified as follows:

$$\frac{\mathrm{d}[^{144}\mathrm{CeY}^-]}{\mathrm{d}t} = k_{\mathrm{Pr,\,app}}[\mathrm{H}^+]\frac{[\mathrm{PrY}^-]_0}{[\mathrm{Pr}^{3+}]_0}[^{144}\mathrm{Ce}^{3+}] - k_{\mathrm{Ce,\,app}}[\mathrm{H}^+][^{144}\mathrm{CeY}^-] \qquad (6)$$

where the subscript $_0$ denotes the initial state. The concentrations of the praseodymium(III) ion and the Pr(III)-EDTA complex remain unchanged during the reaction; therefore, the following relation may be satisfied at equilibrium:

$$K_{\mathrm{app}} = \frac{[\mathrm{PrY}^-]_\mathrm{e}\,[^{144}\mathrm{Ce}^{3+}]_\mathrm{e}}{[\mathrm{Pr}^{3+}]_\mathrm{e}\,[^{144}\mathrm{CeY}^-]_\mathrm{e}} = \frac{k_{\mathrm{Ce,\,app}}}{k_{\mathrm{Pr,\,app}}} \qquad (7)$$

where K_{app} corresponds to the reciprocal of the apparent equilibrium constant of Eq. 2 at a specified acetate concentration, and the subscript e denotes the equilibrium state. The apparent equilibrium constant, K_{app}, was found to be 2.10±0.08 in the presence of 0.04 M acetate at 25°C.

The integration of Eq. 6, then, gives:

$$\ln\left\{\frac{[^{144}\mathrm{CeY}^-]_\mathrm{e}}{[^{144}\mathrm{CeY}^-]_\mathrm{e} - [^{144}\mathrm{CeY}^-]}\right\} = \left\{k_{\mathrm{Pr,\,app}}\frac{[\mathrm{PrY}^-]_0}{[\mathrm{Pr}^{3+}]_0} + k_{\mathrm{Ce,\,app}}\right\}[\mathrm{H}^+]t = k_{\mathrm{app}}\cdot t \ \text{(at a constant pH)} \qquad (8)$$

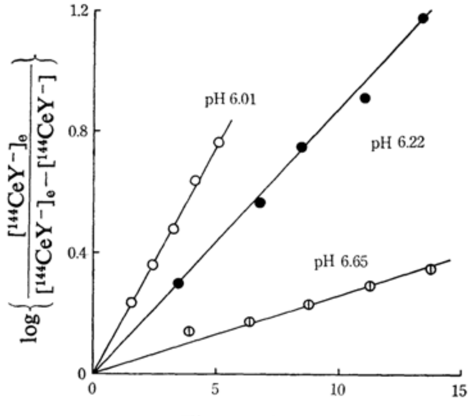

Fig. 1. $\log\left\{\frac{[^{144}\mathrm{CeY}^-]_\mathrm{e}}{[^{144}\mathrm{CeY}^-]_\mathrm{e} - [^{144}\mathrm{CeY}^-]}\right\}$ vs. time.

	$[\mathrm{PrY}^-]_0$	$[\mathrm{Pr}^{3+}]_0$
○ and ●:	1.82×10^{-4} M;	7.62×10^{-5} M
⦶ :	9.52×10^{-5} M;	7.62×10^{-5} M

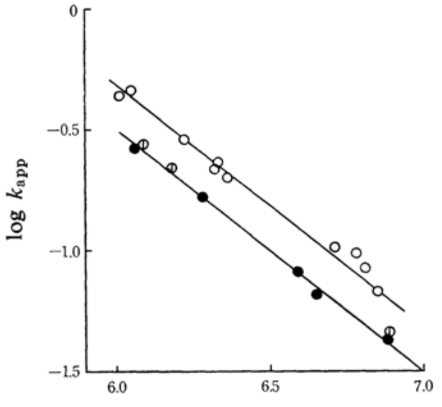

Fig. 2. Dependence of apparent rate constant, k_{app}, on pH at 25°C.

	$[\mathrm{PrY}^-]_0$	$[\mathrm{Pr}^{3+}]_0$
○:	1.82×10^{-4} M;	8.00×10^{-5} M
●:	9.52×10^{-5} M;	7.62×10^{-5} M
⦶:	1.82×10^{-4} M;	1.64×10^{-4} M

Typical plots of the logarithmic term in Eq. 8 against t are shown in Fig. 1. The zero-time exchange appears to be negligible. The apparent rate constant, k_{app}, is obtained from the slope of the straight line shown in Fig. 1. The dependence of $\log k_{\mathrm{app}}$ on pH is given in Fig. 2, indicating the first order dependence of k_{app} on the hydrogen ion concentration. Equation 7 also gives the relation:

$$k_{\mathrm{Ce,\,app}} = K_{\mathrm{app}}\cdot k_{\mathrm{Pr,\,app}} = 2.10k_{\mathrm{Pr,\,app}} \qquad (7')$$

indicating that the exchange rate constants are in inverse order with regard to the stability constants of the EDTA complexes. Hence, as long as the substitution mechanism proposed

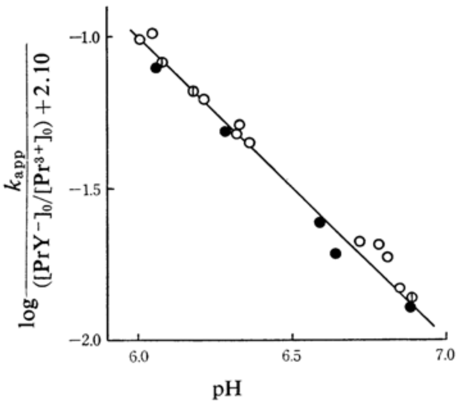

Fig. 3. $\log \frac{k_{app}}{([PrY^-]_0/[Pr^{3+}]_0)+2.10}$ vs. pH.

is valid, the plot of $\log k_{app}/\{([PrY^-]_0/[Pr^{3+}]_0)+2.10\}$ against the pH value must normalize the experimental values obtained under different conditions, giving a straight line with a unit slope. The value of $k_{Pr,\,app}$ can be determined from the intercept. The results are satisfactory, as Fig. 3 shows, and lend support to the kinetic mechanism proposed. The exchange rate constant, $k_{Pr,\,app}$, was determined to be:

$$k_{Pr,\,app}=1.0_1\times10^5\ \text{l. mol}^{-1}\text{min}^{-1}$$

and from the relation expressed by Eq. 7′, $k_{Ce,\,app}$ was calculated as follows:

$$k_{Ce,\,app}=2.1_1\times10^5\ \text{l. mol}^{-1}\ \text{min}^{-1}$$

The Chemical Behavior of ^{144}Pr.—In order to estimate the contribution of the thermal exchange reaction, the dependence of the $^{144}PrY^-$-yield on the pH value was investigated. As is shown in Fig. 4, the $^{144}PrY^-$-yield decreases gradually with the pH, indicating that the departure from the equilibrium value is large in higher pH regions.

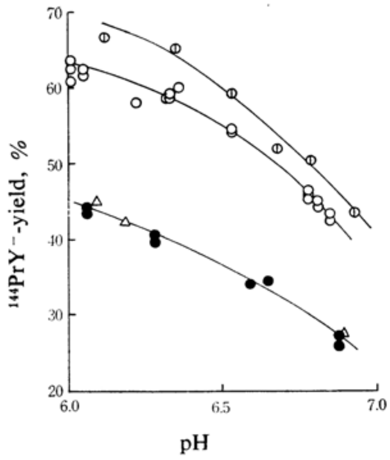

Fig. 4. Dependence of the $^{144}PrY^-$-yield on pH at 25°C.

	$[PrY^-]_0$	$[Pr^{3+}]_0$
⦶ :	2.40×10^{-4} M;	8.00×10^{-5} M
○ :	1.82×10^{-4} M;	7.62×10^{-5} M
● :	9.52×10^{-5} M;	7.62×10^{-5} M
△ :	1.82×10^{-4} M;	1.64×10^{-4} M

If the ^{144}Pr atoms which escape from the parent molecule distribute thermally between the praseodymium(III) ion and the Pr(III)-EDTA complex, the fraction of exchange that has taken place during the time, t, can be expressed as:

$$\ln\left\{\frac{[^{144}PrY^-]_e}{[^{144}PrY^-]_e-[^{144}PrY^-]}\right\}=k_{Pr,\,app}\left\{\frac{[Pr^{3+}]_0+[PrY^-]_0}{[Pr^{3+}]_0}\right\}[H^+]t \quad (9)$$

Of course, one must take into consideration the fact that, even in the case of the transformation of the ^{144}Ce(III)-EDTA complex to the ^{144}Pr(III)-EDTA complex without any net chemical change, a re-distribution of the praseodymium ions takes place because of the difference in the formation constants of their EDTA complexes.

First, let us assume that the extent of the bond-rupture by the β^--decay process is insensitive to the pH, viz., that t in Eq. 9 is a constant. When one plots the logarithmic fraction of the exchange vs. the pH, a straight line with a slope of -1 should be obtained. On the other hand, the value of t in Eq. 9 can be determined by introducing the rate constants obtained in the preceding section. These results are given in Figs. 5 and 6. The non-unit slope, as shown in Fig. 5, means that the extent of formation of free ^{144}Pr ions varies with the pH; that is, the reaction time

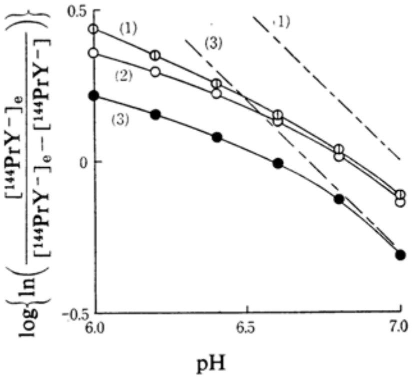

Fig. 5. $\log\left\{\ln\left(\frac{[^{144}PrY^-]_e}{[^{144}PrY^-]_e-[^{144}PrY^-]}\right)\right\}$ vs. pH.

	$[PrY^-]_0$	$[Pr^{3+}]_0$
⦶ :	2.40×10^{-4} M;	8.00×10^{-5} M
○ :	1.82×10^{-4} M;	7.62×10^{-5} M
● :	9.52×10^{-5} M;	7.62×10^{-5} M

The dashed lines were calculated by Eq. 9.

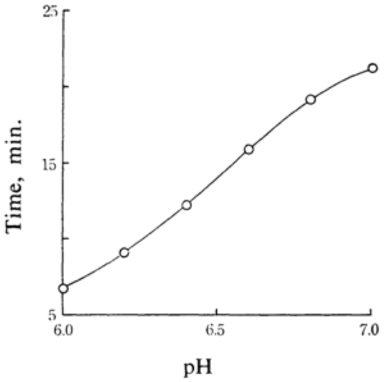

Fig. 6. Reaction time vs. pH.
$[\text{PrY}^-]_0=1.82\times10^{-4}$ M
$[\text{Pr}^{3+}]_0=7.62\times10^{-5}$ M

is not constant. However, even if the concept that the extent of bond rupture is sensitive to pH is valid, the values of the reaction time obtained are fairly small in the lower pH region, as compared with the average life of ^{144}Pr, τ, which is defined as:

$$\tau=t_{1/2}/0.693=25.3\ \text{min.}$$

These facts are strong evidence in support of the presence of an intermediate with a measurable lifetime produced by the β^--decay of the ^{144}Ce(III)-EDTA complex.

Before we consider the physical and chemical meanings of the intermediate complex, an attempt to treat the decomposition of this complex on the basis of kinetics will be discussed. The deviation of the ^{144}PrY$^-$-yield from the equilibrium values leads to an assumption that the irreversible decomposition of the intermediate complex to produce the free ^{144}Pr ions is promoted by the action of either hydroxide ions or protonated EDTA anions (HY^{3-}), which are supplied steadily by the acid-catalyzed dissociation of the Pr(III)-EDTA complex. The latter mechanism is substantially analogous to the decomposition of the Mn-(III)-EDTA complex in the presence of an excess of EDTA.[4] The proposed mechanism excludes a direct bimolecular reaction between the intermediate and Pr(III)-EDTA complex to afford ^{144}Pr-EDTA complex, because ^{144}Pr atoms were considerably enriched in the free-ion fraction. Hence, the decomposition process may be expressed as:

$$^{144}\text{PrZ}\xrightarrow[k_1]{\text{OH}^-,\ \text{HY}^{3-}}{}^{144}\text{Pr}^{3+}\underset{k_2}{\rightleftarrows}{}^{144}\text{PrY}^- \tag{10}$$

where ^{144}PrZ represents the intermediate complex.

The fraction of the ^{144}Pr(III)-EDTA complex, Z, at the time, t, can be obtained by the following equation:

$$Z=\frac{[\text{PrY}^-]_0}{([\text{Pr}^{3+}]_0+[\text{PrY}^-]_0)2\sqrt{\alpha^2-\beta}}\times\left(r_2e^{r_1t}-r_1e^{r_2t}+2\sqrt{\alpha^2-\beta}\right) \tag{11}$$

where:

$$k_1+k_2=2\alpha,\quad k_1k_2=\beta$$
$$r_1=-\alpha+\sqrt{\alpha^2-\beta}\quad r_2=-\alpha-\sqrt{\alpha^2-\beta}$$
$$k_1=k'[\text{OH}^-]+k''[\text{H}^+][\text{PrY}^-]_0/[\text{Pr}^{3+}]_0 \tag{12}$$
$$k_2=k_{\text{Pr, app}}[\text{H}^+]([\text{Pr}^{3+}]_0+[\text{PrY}^-]_0)/[\text{Pr}^{3+}]_0$$

k' and k'' are the rate constants for the hydroxide ion- and the protonated EDTA anion-dependent terms respectively. If one chooses suitable values for k' and k'', the ^{144}PrY$^-$-yield can be calculated from Eqs. 9 and 11, provided that the ^{144}Pr atoms produced by the β^--decay of free ^{144}Ce(III) ions are reduced instantaneously to stable ^{144}Pr(III) ions through electron-transfer with surrounding substances.

By using the rate constants, $k'=10^{6.1}$ l. mol$^{-1}\cdot$min^{-1} and $k''=10^{4.4}$ l. mol^{-1} min^{-1}, and the reaction time of $t=25.3$ min., the ^{144}PrY$^-$-yields were calculated as in Fig. 7. The agreement between the observed and calculated ^{144}PrY$^-$-yields is satisfactory.

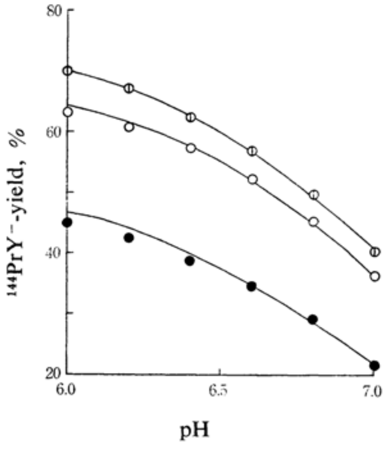

Fig. 7. The ^{144}PrY$^-$-yield calculated by Eqs. 9 and 11.

	$[\text{PrY}^-]_0$	$[\text{Pr}^{3+}]_0$
⦶ :	2.40×10^{-4} M ;	8.00×10^{-5} M
○ :	1.82×10^{-4} M ;	7.62×10^{-5} M
● :	9.52×10^{-5} M ;	7.62×10^{-5} M

The circles indicate the experimental values obtained from the curves in Fig. 4.
The solid curves were calculated by Eqs. 9 and 11.

To confirm this mechanism, a similar experiment was carried out with the cerium(III) ion and Ce(III)-EDTA complex system. The

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[4] K. A. Schroeder and R. E. Hamm, *Inorg. Chem.*, 3, 391 (1964).

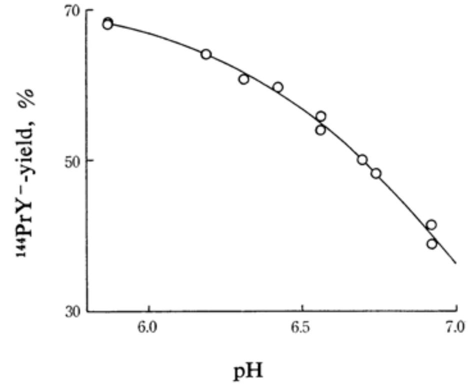

Fig. 8. Dependence of the ^{144}PrY$^-$-yield on pH at 25°C in the Ce^{3+}-CeY^- system.
$[CeY^-]_0=1.00\times10^{-4}$ M;
$[Ce^{3+}]_0=8.08\times10^{-5}$ M

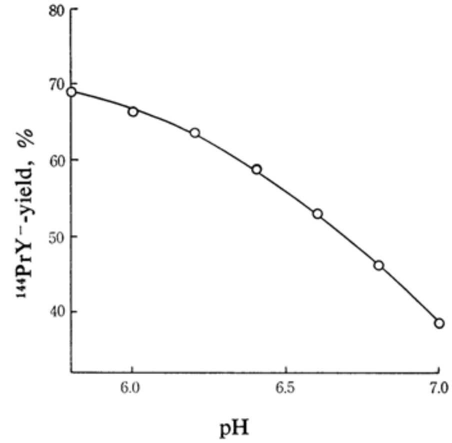

Fig. 9. The ^{144}PrY$^-$-yield calculated by Eqs. 13 and 14.
$[CeY^-]_0=1.00\times10^{-4}$ M;
$[Ce^{3+}]_0=8.08\times10^{-5}$ M
○ indicates the experimental value obtained from the curve in Fig. 8.
The solid curve was calculated by Eqs. 13 and 14.

relation between the ^{144}PrY$^-$-yield and the pH is shown in Fig. 8. The substitution reaction for a ^{144}Pr(III) ion and a Ce(III)-EDTA complex is expressed as follows:

$$\ln\left\{\frac{[^{144}\mathrm{PrY}^-]_e}{[^{144}\mathrm{PrY}^-]_e-[^{144}\mathrm{PrY}^-]}\right\}=\left\{k_{\mathrm{Ce,\,app}}\frac{[\mathrm{CeY}^-]_0}{[\mathrm{Ce}^{3+}]_0}+k_{\mathrm{Pr,\,app}}\right\}[\mathrm{H}^+]t \qquad (13)$$

In this system, Eq. 11 will be rewritten as:

$$Z=\frac{2.10[\mathrm{CeY}^-]_0}{([\mathrm{Ce}^{3+}]_0+2.10[\mathrm{CeY}^-]_0)2\sqrt{\alpha^2-\beta}}\times(r_2e^{r_1t}-r_1e^{r_2t}+2\sqrt{\alpha^2-\beta}) \qquad (14)$$

and the rate constants for the processes in Eq. 10 are expressed, respectively, as follows:

$$k_1=k'[\mathrm{OH}^-]+2.10k''[\mathrm{H}^+][\mathrm{CeY}^-]_0/[\mathrm{Ce}^{3+}]_0$$

$$k_2=\{k_{\mathrm{Ce,\,app}}[\mathrm{CeY}^-]_0/[\mathrm{Ce}^{3+}]_0+k_{\mathrm{Pr,\,app}}\}[\mathrm{H}^+] \qquad (15)$$

As Fig. 9 shows, the excellent agreement between the ^{144}PrY$^-$-yield calculated by Eqs. 13 and 14 and the experimental values further supports the proposed decomposition process of the intermediate complex.

These results indicate that at least the intermediate can not be regarded as the EDTA complex, the chemical behavior of which is treated reasonably by Eq. 9 or Eq. 13. EDTA is a reducing agent, one which reduces permanganate, chromate and cerium(IV) ions in an acidic solution,[5] but EDTA bound in a metal complex is not oxidized by permanganate ions.[6] Recently, it has been found that the photodecomposition of acid aquoethylenediaminetetraacetatoferrate(III) produces both iron(II) ions by electron-transfer and carbon dioxide by the decarboxylation of a coordinated carboxylate group.[7] Schroeder and Hamm[4] also found that carbon dioxide and formaldehyde were produced in the case of the decomposition of the Mn(III)-EDTA complex. By taking into consideration the fact that the praseodymium(IV) ion is very unstable in solution, it is apparent that an intramolecular electron-transfer between the tetravalent praseodymium and the EDTA molecule will take place at the time of the β^--decay of ^{144}Ce complexed with EDTA, as has been proposed in the previous paper.[2] The trivalent ^{144}Pr ion remains complexed with an oxidized EDTA radical, which is probably produced by the loss of one chelating carboxylate group; it does not escape from the molecule.

According to the formation constant of the cerium(III) acetate complex,[8] about 80 per cent of the cerium(III) ions complex with acetate ions under the experimental conditions. The tetravalent praseodymium produced by the β^--decay of the ^{144}Ce acetate complex may be either reduced by the intramolecular electron-transfer or by the action of the surrounding substances. The reduced praseodymium(III) ion will escape easily from the molecule, because the acetate ion is a monodentate ligand and it forms labile complexes with praseodymium(III) ions. The process of the deactivation of the ^{144}Pr produced by the β^--decay of ^{144}Ce is illustrated schematically in Fig. 10.

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[5] P. N. Palei and N. I. Udal'tsova, *Zhur. Anal. Khim.*, **15**, 668 (1960); *Chem. Abstr.*, **55**, 18424 (1961).

[6] M. J. Beck, *Chemist-Analyst*, **50**, 14 (1961).

[7] J. K. Lambert, C. E. Godsey and L. M. Seitz, *Inorg. Chem.*, **2**, 127 (1963).

[8] S. K. Kolat and J. E. Powell, ibid., **1**, 293 (1962).

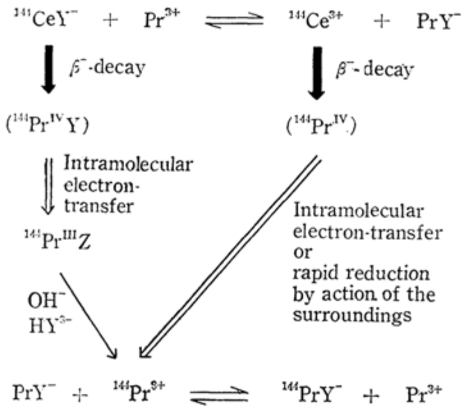

Fig. 10. De-activation proceses of ^{144}Pr atom produced by β^--decay of ^{144}Ce in the EDTA complex system.

A satisfactory explanation for the experimental results can be offered on the assumption that all the decay events of the complexed ^{144}Ce lead to the formation of the intermediate. Nevertheless, the excited ^{144}Pr atoms may be stabilized by a different route; namely, the multiple charging due to internal conversion, at least in part, may cause an exhaustive decomposition, thus liberating the free ^{144}Pr ion. It must be noted, therefore, that the values obtained for the rate constants, k' and k'', are not absolute, but include the various accompanying effects resulting from the β^--decay process.

Summary

The substitution reaction of ^{144}Ce(III) ions with the ^{144}Pr(III)-EDTA complex in an aqueous solution at 25°C has been investigated; the rate-determining step has been found to be the acid-catalyzed dissociation of the Pr(III)-EDTA complex.

On the basis of the above substitution mechanism, the chemical behavior of the ^{144}Pr atoms produced by the β^--decay of ^{144}Ce has been satisfactorily explained in terms of a model which involves the formation of an intermediate complex. The kinetic treatment leads to the conclusion that the intermediate, produced as a results of an increase in the nuclear charge by the β^--decay of the complexed ^{144}Ce, is available for attack by hydroxide ions and protonated EDTA anions and, consequently, produces free ^{144}Pr(III) ions.

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