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Chemical Effects Associated with the β-Decay Process. V. Kinetic Studies of the Chemical Behavior of the ^{144}Pr Formed by the Decay of the ^{144}Ce(III)-Ethylenediaminetetraacetate and ^{144}Ce(III)-*trans*-1,2-Diaminocyclohexane-*N*,*N'*-tetraacetate

Takanobu SHIOKAWA, Hiroaki KIDO and Takashi OMORI

Department of Chemistry, Faculty of Science, Tohoku University, Katahira, Sendai

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The chemical effects associated with the β^--decay of ^{144}Ce(III)-aminopolycarboxylate complexes have been further investigated. The chemical behavior of ^{144}Pr was analyzed kinetically on the basis of the isotopic exchange-reaction mechanism. The formation of the intermediate complex produced by an intramolecular electron transfer of the ^{144}Pr(IV)-aminopolycarboxylate following the β^--decay of ^{144}Ce(III) complex was also confirmed. In the ethylenediaminetetraacetate and *trans*-1,2-diaminocyclohexane-*N*,*N'*-tetraacetate systems, the values for the bond-rupture of the daughter complex ions are fairly much larger than in the diethylenetriaminepentaacetate system, suggesting that a kinetically-excited intermediate complex decomposes to a free ion to some extent.

In the β^--decay of the ^{144}Ce(III)-ethylenediaminetetraacetate(^{144}Ce(III)-EDTA) complex, the formation of an intermediate complex has been proposed on the basis of kinetic treatments.[1,2] Further investigation of the ^{144}Ce(III)-diethylenetriaminepentaacetate(^{144}Ce(III)-DTPA) complex revealed that an exhaustive bond-rupture of the daughter complex ion involves 25 per cent of the ^{144}Pr formed by the decay of the parent complex.[3]

Recently, Glentworth and Wright[4] have reported on the chemical behavior of ^{144}Pr/^{143}Pr in the aminopolycarboxylate complexes, and have proposed that a substantial fraction of the break-up of ^{144}Pr/^{143}Pr results in the multiple charging of the daughter complex as a result of the internal conversion of γ-rays and electron shake-off, as has already been pointed out in our previous papers.[2,3] However, the deactivation processes do not seem to have been established.

In order to confirm the stabilization process of ^{144}Pr on the basis of our model, the chemical behavior of ^{144}Pr was investigated in the ^{144}Ce(III)-*trans*-1,2-diaminocyclohexane-*N*,*N'*-tetraacetate (^{144}Ce(III)-DCTA) complex system. Furthermore, some additional experiments in the EDTA complex system were carried out.

Experimental

G.R.-grade EDTA and DCTA were used without further purification. The chelating agent solutions were standardized against a standard zinc(II) solution by volumetric titration, using Eriochrome Black T as an indicator. All the other chemicals and the experimental procedures employed here were substantially the same as those described previously.[2]

Results

Isotopic Exchange Reaction. Kinetic experiments on the exchange reaction,

$$^{144}\mathrm{Ce}^{3+} + \mathrm{CeY}^- \rightleftarrows {}^{144}\mathrm{CeY}^- + \mathrm{Ce}^{3+} \qquad (1)$$

in the pH range from 4 to 7 at 25°C and at 5°C were carried out; here, Y^{4-} indicates the tetravalent EDTA and DCTA anions. The exchange rate between the uncomplexed cerium(III) ion and cerium(III)-aminopolycarboxylate can be expressed as follows:

For the EDTA complex system:

$$R = k_{\mathrm{Ce}}[\mathrm{H}^+][\mathrm{CeY}^-] \qquad (2)$$

For the DCTA complex system:

$$R = k_{\mathrm{Ce}}[\mathrm{H}^+][\mathrm{CeY}^-] + k'_{\mathrm{Ce}}[\mathrm{CeY}^-] \qquad (3)$$

The isotopic exchange rate constants, k_{Pr} and k'_{Pr}, for the analogous systems of praseodymium(III) have also been calculated using the equilibrium constant, K, for the substitution reaction[3]:

$$^{144}\mathrm{Ce}^{3+} + \mathrm{PrY}^- \rightleftarrows {}^{144}\mathrm{CeY}^- + \mathrm{Pr}^{3+} \qquad (4)$$

The equilibrium constants, K, were obtained as 0.47_7 for the EDTA complex system and 0.47_2 for the DCTA complex system. The isotopic exchange rate constants for these systems are summarized in Table 1.

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

[2] T. Shiokawa and T. Omori, *ibid.*, **38**, 1893 (1965).

[3] T. Shiokawa and T. Omori, *ibid.*, **42**, 696 (1969).

[4] P. Glentworth and C. L. Wright, *J. Inorg. Nucl. Chem.*, **31**, 1263 (1969).

Table 1. Isotopic exchange reaction rate constants

		Ce	Pr
EDTA			
k ($l\cdot$ mol$^{-1}\cdot$ min^{-1})	25°C	2.1×10^5	1.0×10^5
	5°C	4.7×10^4	2.1×10^4
DCTA			
k ($l\cdot$ mol$^{-1}\cdot$ min^{-1})	25°C	$5.7_5\times10^3$	2.7×10^3
	5°C	7.8×10^2	3.7×10^2
k' (min^{-1})	25°C	8.3×10^{-3}	3.9×10^{-3}
	5°C	5.5×10^{-4}	2.6×10^{-4}

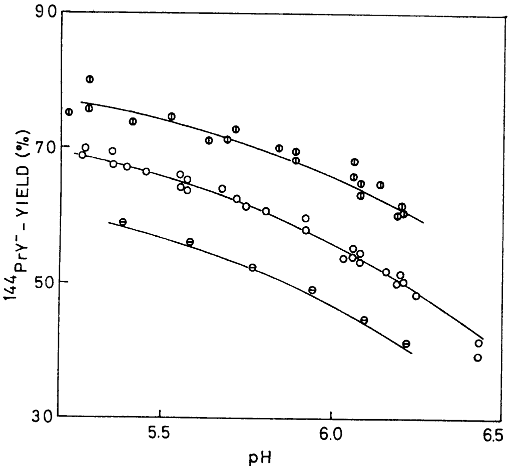

Fig. 1. Dependence of the ^{144}PrY$^-$-yield on pH at 25°C in the EDTA complex system.

	[Ce^{3+}]	[CeY$^-$]
⦶:	1.21×10^{-4} M;	1.00×10^{-4} M
○:	0.808×10^{-4} ;	1.00×10^{-4}
⊖:	0.808×10^{-4} ;	1.50×10^{-4}

Solid curves were calculated by Eq. (11).

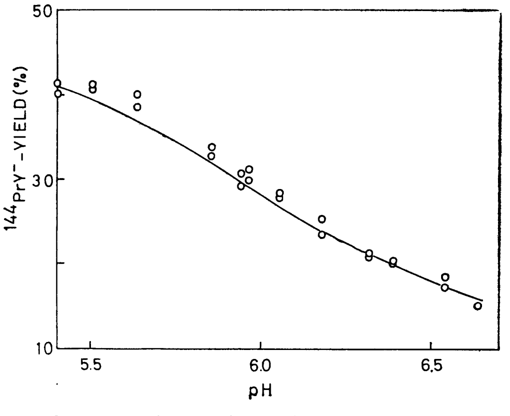

Fig. 2. Dependence of the ^{144}PrY$^-$-yield on pH at 5°C in the EDTA complex system.

[Pr^{3+}]=[PrY$^-$]=1.14×10^{-4} M

Solid curve was calculated by Eq. (11).

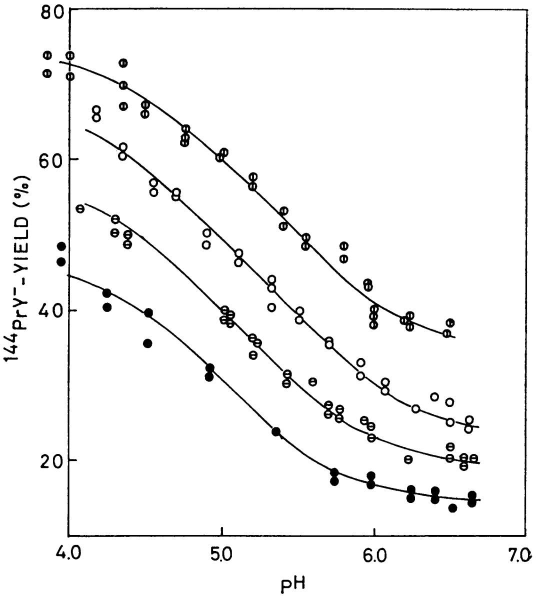

Fig. 3. Dependence of the ^{144}PrY$^-$-yield on pH at 25°C in the DCTA complex system.

	[Ce^{3+}]	[CeY$^-$]
⦶:	1.00×10^{-4} M;	1.50×10^{-4} M
○:	1.00×10^{-4} ;	1.00×10^{-4}
⊖:	1.50×10^{-4} ;	1.00×10^{-4}

●: [Pr^{3+}]=[PrY$^-$]=1.00×10^{-4} M

Solid curves were calculated by Eq. (11).

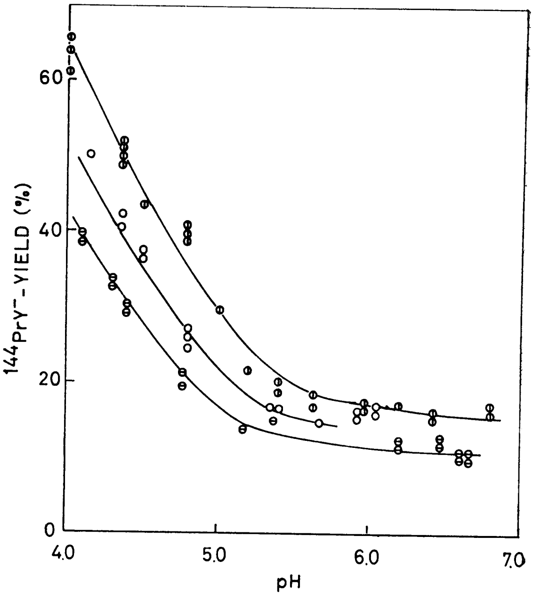

Fig. 4. Dependence of the ^{144}PrY$^-$-yield on pH at 5°C in the DCTA complex system.

	[Ce^{3+}]	[CeY$^-$]
⦶:	1.00×10^{-4} M;	1.50×10^{-4} M
○:	1.00×10^{-4} ;	1.00×10^{-4}
⊖:	1.50×10^{-4} ;	1.00×10^{-4}

Solid curves were calculated by Eq. (11).

Chemical Behavior of ^{144}Pr. After complete equilibration with respect to ^{144}Ce in the systems represented by Eqs. (1) and (4) had been attained chemically, the yield of ^{144}Pr(III)-aminopolycarboxylate (^{144}PrY$^-$-yield) was obtained as a function of pH at 25° and 5°C. The ^{144}PrY$^-$-yield is defined as the ratio of the γ-activity of the eluate to the total γ-activity. The results are shown in Figs. 1—4. In these experiments, the praseodymium ions are carrier-free when the carriers of the Ce(III) ion and Ce(III)-aminopolycarboxylate exist in aqueous solutions, and *vice versa*.

In both the systems, the ^{144}PrY$^-$-yield decreases gradually with the pH, while in the DCTA complex system it seems to be constant in the higher pH regions. On the contrary, all the ^{144}PrY$^-$-yield curves in the lower pH region exhibit asymptotic approaches to the equilibrium values, as is to be expected from the equilibrium constants of Reaction (4).

Discussion

The chemical behavior of the ^{144}Pr formed by the decay of ^{144}Ce(III)-DTPA was successfully explained on the basis of kinetic considerations as follows.[3] The praseodymium(IV)-DTPA complex was promptly reduced by an intramolecular electron-transfer. The trivalent ^{144}Pr, which remains complexed with a degradated DTPA radical, decomposes to a free ion by the dissociation in the substitution reaction. The uncomplexed ^{144}Pr(III) ion is also produced directly by an exhaustive decomposition of the daughter complex ion, without any formation of the intermediate. These stabilization processes of ^{144}Pr are considered to be valid also in the aminopolycarboxylate complex systems studied in this paper. Thus, the chain reactions for the stabilization of ^{144}Pr can be expressed as follows:

$$\begin{tikzcd}
{}^{144}\mathrm{Ce}^{3+} \arrow[r, "\lambda_{\mathrm{Ce}}"] \arrow[dd, "\underline{\lambda_{\mathrm{Ce}}N_1}", "\lambda_{\mathrm{CeY}}"'] & {}^{144}\mathrm{Pr}^{3+} \arrow[r, "\lambda_{\mathrm{PrY}}"] \arrow[d, "\lambda_{\mathrm{Pr}}"] & {}^{144}\mathrm{PrY}^{-} \arrow[d, "\lambda_{\mathrm{Pr}}"] & \\
 & \underline{\lambda_{\mathrm{Pr}}N_2} & \underline{\lambda_{\mathrm{Pr}}N_3} & \\
{}^{144}\mathrm{CeY}^{-} \arrow[r, "(1-\alpha)\lambda_{\mathrm{Ce}}"] \arrow[ddr, "\alpha\lambda_{\mathrm{Ce}}"'] & {}^{144}\mathrm{Pr(III)Z} \arrow[r, "\lambda_d"] \arrow[d, "\lambda_{\mathrm{Pr}}"] & {}^{144}\mathrm{Pr}^{3+} \arrow[r, "\lambda_{\mathrm{PrY}}"] \arrow[d, "\lambda_{\mathrm{Pr}}"] & {}^{144}\mathrm{PrY}^{-} \arrow[d, "\lambda_{\mathrm{Pr}}"] \\
 & \underline{\lambda_{\mathrm{Pr}}N_4} & \underline{\lambda_{\mathrm{Pr}}N_5} & \underline{\lambda_{\mathrm{Pr}}N_6} \\
 & {}^{144}\mathrm{Pr}^{3+} \arrow[r, "\lambda_{\mathrm{PrY}}"] \arrow[d, "\lambda_{\mathrm{Pr}}"] & {}^{144}\mathrm{PrY}^{-} \arrow[d, "\lambda_{\mathrm{Pr}}"] & \\
 & \underline{\lambda_{\mathrm{Pr}}N_7} & \underline{\lambda_{\mathrm{Pr}}N_8} &
\end{tikzcd} \tag{6}$$

where λ_{Ce} and λ_{Pr} are the decay constants of ^{144}Ce and ^{144}Pr respectively, where λ_{CeY} and λ_{PrY} denote the respective exchange-rate constants of ^{144}Ce^{3+} and ^{144}Pr^{3+} with the aminopolycarboxylate complex, where λ_d is the decomposition rate constant of the intermediate (^{144}Pr(III)Z), and where α is the ratio of bond-rupture, which is defined as the ratio of the ^{144}Pr^{3+} produced directly from ^{144}Ce(III)-aminopolycarboxylate without any formation of the intermediate possessing a finite life-time.

In Eq. (6), the fractions of $\lambda_{\mathrm{Pr}}N_3$, $\lambda_{\mathrm{Pr}}N_4$, $\lambda_{\mathrm{Pr}}N_6$, and $\lambda_{\mathrm{Pr}}N_8$ give the ^{144}PrY$^-$-yield, supposing that, upon separation, the intermediate complex is not adsorbed on the ion-exchange resin. When the chemical equilibrium with respect to ^{144}Ce had been attained, and when the ^{144}Pr initially present had decayed out, the ^{144}PrY$^-$-yield was obtained; therefore, the solution of Bateman's equation[5] for the respective fractions are given for the system ascribed by Eq. (1) as follows:

$$\lambda_{\mathrm{Pr}}N_3 = \lambda_{\mathrm{Ce}}N_1 \cdot \frac{\lambda_{\mathrm{PrY}}}{\lambda_{\mathrm{Pr}}+\lambda_{\mathrm{PrY}}} \cdot \frac{[\mathrm{Ce}^{3+}]_e}{[\mathrm{Ce}^{3+}]_e+[\mathrm{CeY}^-]_e} \times \frac{[{}^{144}\mathrm{PrY}^-]_e}{[{}^{144}\mathrm{Pr}^{3+}]_e+[{}^{144}\mathrm{PrY}^-]_e} \tag{7}$$

$$\lambda_{\mathrm{Pr}}N_4 = \lambda_{\mathrm{Ce}}N_1 \cdot \frac{(1-\alpha)\lambda_{\mathrm{Pr}}}{\lambda_{\mathrm{Pr}}+\lambda_d} \cdot \frac{[\mathrm{CeY}^-]_e}{[\mathrm{Ce}^{3+}]_e+[\mathrm{CeY}^-]_e} \tag{8}$$

$$\lambda_{\mathrm{Pr}}N_6 = \lambda_{\mathrm{Ce}}N_1 \cdot \frac{(1-\alpha)\lambda_{\mathrm{PrY}}\lambda_{\mathrm{d}}}{(\lambda_{\mathrm{Pr}}+\lambda_{\mathrm{PrY}})(\lambda_{\mathrm{Pr}}+\lambda_{\mathrm{d}})} \times \frac{[\mathrm{CeY}^-]_e}{[\mathrm{Ce}^{3+}]_e+[\mathrm{CeY}^-]_e} \cdot \frac{[{}^{144}\mathrm{PrY}^-]_e}{[{}^{144}\mathrm{Pr}^{3+}]_e+[{}^{144}\mathrm{PrY}^-]_e} \tag{9}$$

$$\lambda_{\mathrm{Pr}}N_8 = \lambda_{\mathrm{Ce}}N_1 \cdot \frac{\alpha\lambda_{\mathrm{PrY}}}{\lambda_{\mathrm{Pr}}+\lambda_{\mathrm{PrY}}} \cdot \frac{[\mathrm{CeY}^-]_e}{[\mathrm{Ce}^{3+}]_e+[\mathrm{CeY}^-]_e} \times \frac{[{}^{144}\mathrm{PrY}^-]_e}{[{}^{144}\mathrm{Pr}^{3+}]_e+[{}^{144}\mathrm{PrY}^-]_e} \tag{10}$$

where the effect of the disintegration of ^{144}Ce can be ignored. For the system expressed by Eq. (4), analogous equations are derived by exchanging the terms involving the concentrations of the metal ions. Thus, the ^{144}PrY$^-$-yield is given by the sum of Eqs. (7)—(10); that is,

$${}^{144}\mathrm{PrY}^-\text{-yield}(\%) = \frac{\lambda_{\mathrm{Pr}}(N_3+N_4+N_6+N_8)}{\lambda_{\mathrm{Ce}}N_1} \times 100 \tag{11}$$

Since the values for λ_{Pr} and λ_{PrY} have already been established, the values for λ_d and α can be obtained by inserting the experimental values for the ^{144}PrY$^-$-yields.

It was found that the ratio of the bond-rupture, α, is a constant independent of the temperature, while the λ_d depends on the temperature and is affected by the concentration of the hydrogen ion;

$$\lambda_d = k_d[\mathrm{H}^+] \tag{12}$$

The values for the decomposition rate constant, k_d, of the intermediate, Pr(III)Z, and for the α thus obtained are summarized in Table 2, together with the data obtained in the DTPA complex system.[3] The experimental and calculated values

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[5] H. Bateman, *Proc. Cambridge Phil. Soc.*, **15**, 423 (1910).

Table 2. Decomposition rate constants of the intermediate complex and ratio of bond-rupture

	k_d* ($l\cdot\text{mol}^{-1}\cdot\text{min}^{-1}$)	α
EDTA (25°C)	$(2.5\pm1)\times10^5$	0.7
(5°C)	$(5\pm2)\times10^4$	
DCTA (25°C)	$(3\pm1)\times10^4$	0.75
(5°C)	$(8\pm3)\times10^3$	
DTPA (25°C)	$(5\pm2)\times10^4$	0.25
(5°C)	$(2\pm1)\times10^4$	

* $\lambda_d = k_d[H^+]$

for the $^{144}PrY^-$-yields are compared in Figs. 1—4.

The bond rupture of the daughter complex may be caused by the formation of a multiply-charged ^{144}Pr ion due to electron shake-off and the internal conversion of γ-rays, followed by the Auger process. In the DTPA-complex system, the ratio of the bond rupture of 0.25 corresponds to the extent of the formation of the multiply-charged ^{144}Pr ion. In the EDTA- and DCTA-complex systems, the ratios of the bond rupture of 0.70 and 0.75 respectively are much larger than that in the DTPA complex system, indicating that there is involved another process, without any formation of a stable intermediate. This process may be accounted possibly by the recoil effect. In the β^--decay of ^{144}Ce, the recoil energies imparted to free ^{144}Pr atoms range from 0 to 1.6 eV. The probability of bond rupture as a result of recoil only is very small; however, a significant fraction of the β^--decay of ^{144}Ce would leave the daughter complex in a kinetically-excited state. Thus, by taking into consideration the fact that the activation energies for the decomposition of the intermediate are estimated to be about 10 kcal/mol, it is reasonable that the kinetically-excited decomposition of the intermediate should take place, resulting in the formation of the uncomplexed $^{144}Pr(III)$ ion.

In the DTPA-complex system, the kinetically-excited decomposition of the intermediate was not observed. The differences in the chemical behavior of ^{144}Pr in the DTPA complex system from that in the EDTA and DCTA complex systems may be attributed to the difference in the molecular structures of the chelates; that is, the EDTA and DCTA are hexadentate chelating agents, while the DTPA is an octadentate.

In view of the decomposition mechanism and rate constants, the stabilization processes of ^{144}Pr proposed in the DTPA-complex system[3)] are further confirmed in the EDTA- and DCTA-complex systems. In addition, a new process of the kinetically-excited decomposition of the intermediate is proposed. The stabilization processes of ^{144}Pr are shown schematically in Fig. 5.

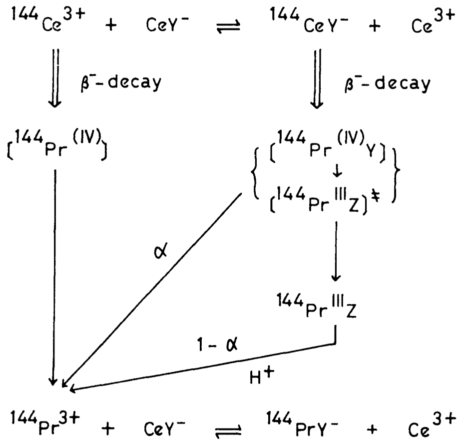

Fig. 5. Stabilization processes of ^{144}Pr produced by β^--decay of ^{144}Ce in the aminopolycarboxylate complex system.