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# Chemical Effects Associated with $\beta$-Decay Process. IV. Kinetic Studies of the Chemical Behavior of $^{144}$Pr Decayed from the $^{144}$Ce(III)-Diethylenetriaminepentaacetate Complex

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The chemical behavior of $^{144}$Pr as a result of the $\beta^-$-decay of the $^{144}$Ce(III)-diethylenetriaminepentaacetate ($^{144}$Ce(III)-DTPA) complex was investigated in detail on the basis of the substitution reaction mechanism. The experimental results, represented in terms of the yield of the $^{144}$Pr(III)-DTPA complex, were explained quantitatively by the application of Bateman's equation. An increase in the nuclear charge in the $\beta^-$-decay of the $^{144}$Ce(III)-DTPA complex may result in the formation of $^{144}$Pr(IV)-DTPA, which would then be reduced to an intermediate complex of $^{144}$Pr(III) by an intramolecular electron-transfer. The mechanisms and the rate constants are established for the decomposition of the intermediate leading to the formation of the uncomplexed ion. It was also suggested that the uncomplexed $^{144}$Pr(III) ion is produced directly by an exhaustive bond-rupture of the daughter complex ion, without any formation of the intermediate. The ratio of bond-rupture was determined to be 0.25; this value is in accordance with the theoretical value for the formation of the multiply-charged $^{144}$Pr ion due to electron shake-off and the internal conversion of $\gamma$-rays, followed by the Auger process.

In a previous paper,[1] the chemical behavior of $^{144}$Pr produced by the $\beta^-$-decay of the $^{144}$Ce(III)-EDTA complex was investigated on the basis of kinetic considerations. The kinetic treatment indicated that the decomposition rate of an intermediate complex produced as a result of an increase in the nuclear charge in the $\beta^-$-decay of the $^{144}$Ce(III)-EDTA complex, is very important in determining the yield of the $^{144}$Pr(III)-EDTA complex.

Recently, Glentworth and Wiseall[2] extensively investigated the chemical behavior of $^{144}$Pr in various aminopolycarboxylate complex systems, but the model they proposed does not necessarily account for all of their results.

It appeared necessary to investigate further the stabilization process of $^{144}$Pr decayed from the $^{144}$Ce(III)-aminopolycarboxylate complexes. As the chelating agent, diethylenetriaminepentaacetic acid (DTPA) was chosen, for with it the lanthanide ions form more stable complexes than with EDTA.[3] In the present paper, the chemical behavior of $^{144}$Pr will be discussed in terms of the yield of the $^{144}$Pr(III)-DTPA complex, and on the basis of the exchange reaction mechanisms of both $^{144}$Ce$^{3+}$ and $^{144}$Pr$^{3+}$ with the cerium(III)-DTPA complex in aqueous solutions.

## Experimental

G. R.-grade DTPA was used without further purification. An approximately $10^{-2}$M stock solution of $Na_3H_2$DTPA was prepared by the partial neutralization of the directly-weighed acid with carbonate-free sodium hydroxide. The chelating agent solution was 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.[1]

## Results

**Isotopic Exchange Reaction.** The exchange rates and mechanisms for the following systems were established:

$$^{144}\mathrm{Ce}^{3+} + \mathrm{CeY}^{2-} \rightleftharpoons {}^{144}\mathrm{CeY}^{2-} + \mathrm{Ce}^{3+} \qquad (1)$$

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

where $Y^{5-}$ indicates the pentavalent DTPA anion. The isotopic exchange rate, $R$, between the uncomplexed $^{144}$Ce(III) ion and the cerium(III)-DTPA complex ion in the pH range of 4.8—5.8 can be expressed as:

$$R = k_{\mathrm{Ce}}[\mathrm{H}^+]^2[\mathrm{CeY}^{2-}] \qquad (3)$$

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1) T. Shiokawa and T. Omori, This Bulletin, **38**, 1892 (1965).

2) P. Glentworth and B. Wiseall, "Chemical Effects of Nuclear Transformations," Vol. II, IAEA, Vienna (1965), p. 483.

3) L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," The Chemical Society, London (1964).

Glentworth *et al.*[2] have found that, in the DTPA complex system, the exchange rate is expressed as follows:

$$R = k_{\mathrm{Ce}}[\mathrm{H^+}]^2[\mathrm{CeY^{2-}}] + k'_{\mathrm{Ce}}[\mathrm{Ce^{3+}}][\mathrm{CeY^{2-}}] \qquad (3')$$

However, the contribution to the exchange rate of the second term on the right hand of Eq. (3′) is fairly small and seems to have little importance in a discussion of the reaction mechanism. Therefore, further study was not made of this effect.

When the equilibrium constant, $K$, for the reaction expressed by Eq. (2) and $k_{\mathrm{Ce}}$ for Eq. (3) are known, the rate constant, $k_{\mathrm{Pr}}$, can be calculated by using the following relation[1]:

$$K = \frac{[\mathrm{Pr^{3+}}]_e[\mathrm{^{144}CeY^{2-}}]_e}{[\mathrm{PrY^{2-}}]_e[\mathrm{^{144}Ce^{3+}}]_e} = \frac{k_{\mathrm{Pr}}}{k_{\mathrm{Ce}}} \qquad (4)$$

where the subscript e indicates the chemical equilibrium. The equilibrium constant, $K$, was determined to be $0.28_7$ in the presence of an 0.04M acetate buffer and 0.3M sodium chloride at 25°C. Also, the isotopic exchange rate constants were found to be:

$$k_{\mathrm{Ce}} = 7.7_5 \times 10^8\ \mathrm{l^2mol^{-2}min^{-1}}$$
$$k_{\mathrm{Pr}} = 2.2_3 \times 10^8\ \mathrm{l^2mol^{-2}min^{-1}}$$

**Substitution Reaction of $^{144}$Pr$^{3+}$ with the Ce(III)-DTPA Complex Ion.** According to the results obtained in the preceding section, the rate of the substitution reaction of $^{144}$Pr$^{3+}$ and the cerium(III)-DTPA complex may be expressed as:

$$\ln(1-F) = \ln\left\{\frac{[\mathrm{^{144}PrY^{2-}}]_e - [\mathrm{^{144}PrY^{2-}}]}{[\mathrm{^{144}PrY^{2-}}]_e}\right\} = -\left\{k_{\mathrm{Ce}}\frac{[\mathrm{CeY^{2-}}]}{[\mathrm{Ce^{3+}}]} + k_{\mathrm{Pr}}\right\}[\mathrm{H^+}]^2 t \qquad (5)$$

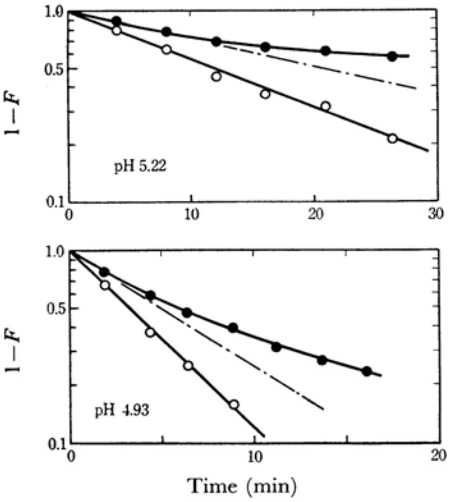

Fig. 1. Relation between $(1-F)$ values and time in the substitution reaction of $^{144}$Pr$^{3+}$ with cerium-(III)-DTPA complex(I).
25°C; $[\mathrm{Ce^{3+}}] = [\mathrm{CeY^{2-}}] = 1.00 \times 10^{-4}$ M
●: $^{144}$Pr; ○: $^{144}$Ce
Dashed lines were calculated by Eq. (5).

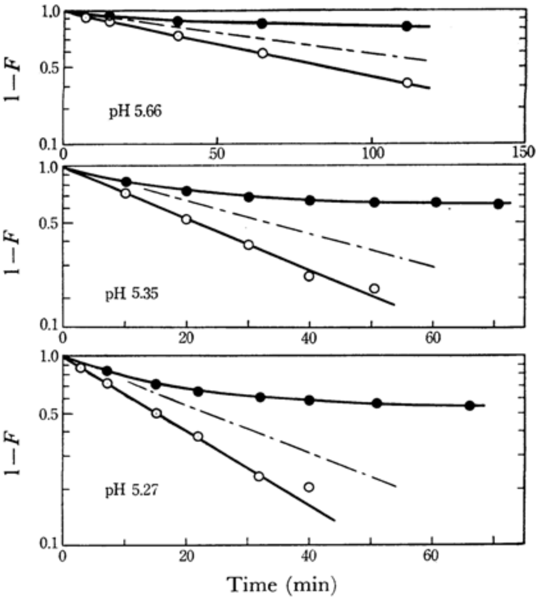

Fig. 2. Relation between $(1-F)$ values and time in the substitution reaction of $^{144}$Pr$^{3+}$ with cerium-(III)-DTPA complex(II).
25°C; $[\mathrm{Ce^{3+}}] = [\mathrm{CeY^{2-}}] = 1.00 \times 10^{-4}$ M
●: $^{144}$Pr; ○: $^{144}$Ce
Dashed lines were calculated by Eq. (5).

where $F$ indicates the fraction of the reaction.

Figures 1 and 2 show plots of the $(1-F)$ values against the reaction time, $t$. In all cases the discrepancy of $(1-F)$ values from those calculated by Eq. (5) increases with the lapse of time. This is partly to be ascribed to the accumulation of the $^{144}$Ce(III)-DTPA complex with the reaction time.

In a previous paper,[1] the chemical behavior of $^{144}$Pr was analyzed satisfactorily by using the average life of $^{144}$Pr as the reaction time; however, the results obtained at pH 4.8 cannot be rigorously explained by using the average life of $^{144}$Pr. It is clearly desirable to introduce a more complete treatment for the stabilization mechanism of $^{144}$Pr.

**The Chemical Behavior of $^{144}$Pr.** After a complete equilibration with respect to $^{144}$Ce had been attained chemically, the $^{144}$PrY$^{2-}$-yield, which is defined as the ratio of the $\gamma$-activity of the eluate to the total activity, was obtained at 25 and 5°C. As is shown in Figs. 3 and 4, the $^{144}$PrY$^{2-}$-yield curves have characteristic shapes in comparison with those obtained in the EDTA complex system.[1] The $^{144}$PrY$^{2-}$-yield at 25°C decreases abruptly up to pH 5.6, while above this point it increases gradually with the pH. At 5°C the minimum point in the $^{144}$PrY$^{2-}$-yield curve would shift to the lower pH region, and above pH 5.6 the $^{144}$PrY$^{2-}$-yields are higher than those at 25°C.

It should be noted that, throughout the investigated pH range, the $^{144}$PrY$^{2-}$-yields obtained

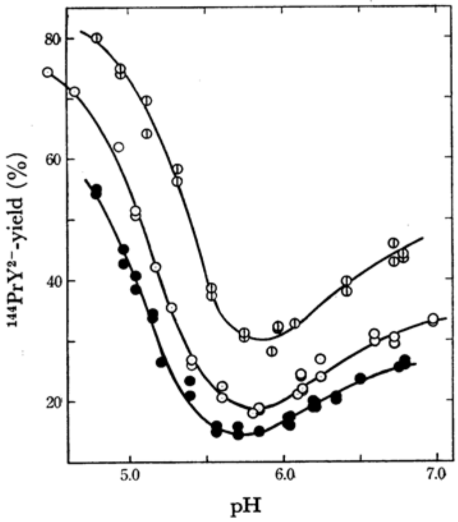

Fig. 3. Dependence of the $^{144}PrY^{2-}$-yield on pH at 25°C.

| | $[CeY^{2-}]$ | $[Ce^{3+}]$ |
|---|---|---|
| ⦶: | $2.50\times10^{-4}$ M | $1.00\times10^{-4}$ M |
| ○: | $1.00\times10^{-4}$ M | $1.00\times10^{-4}$ M |
| ●: | $1.00\times10^{-4}$ M | $1.50\times10^{-4}$ M |

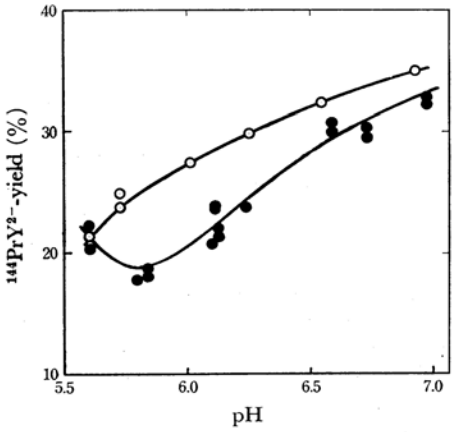

Fig. 4. Dependence of the $^{144}PrY^{2-}$-yield on pH at 5°C.
$[CeY^{2-}] = [Ce^{3+}] = 1.00\times10^{-4}$ M
○: 5°C; ●: 25°C

are less than the equilibrium values to be expected from the relation expressed by Eq. (4).

**Chemical Properties of Ce(IV)-DTPA and Its Reduced Complexes.** Although a knowledge of the chemical properties of the $^{144}Pr(IV)$-DTPA complex is necessary, the higher oxidation potential $Pr^{3+}$ to $Pr^{4+}$, reported to be $-2.86$ V,[4] makes this subject difficult to investigate. Thus, some experiments have been carried out on the cerium(IV)-DTPA complex system, on the supposition that the results obtained may be applicable to the $^{144}Pr(IV)$-DTPA complex system.

The absorption spectra of the cerium(IV)-DTPA complex and its reduced complex are shown in Fig. 5, together with that of the cerium(III)-DTPA complex. Spectrophotometric investigation showed that the cerium(IV)-DTPA complex is relatively stable in the dark. The decomposition rate is first order with respect to the concentration of the cerium(IV)-DTPA complex. A slight dependence of the rate on the concentration of the hydrogen ion was observed above pH 4.5. The apparent rate constant was obtained as $10^{-2.6}$ $min^{-1}$ at 25°C in the dark.

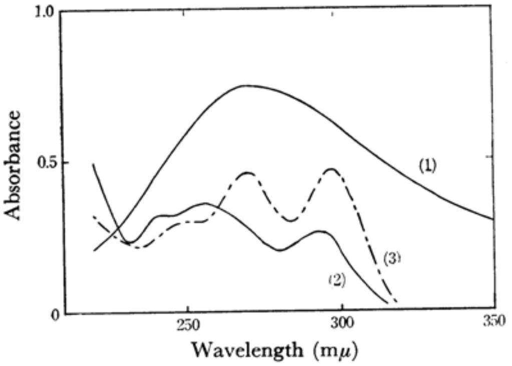

Fig. 5. Absorption spectra of cerium complexes.
(1) Ce(IV)-DTPA ($1.00\times10^{-4}$ M)
(2) Ce(III)Z ($8.00\times10^{-4}$ M)
(3) Ce(III)-DTPA ($8.00\times10^{-4}$ M)

The cerium(III) complex with an oxidation product of DTPA, Ce(III)Z, is stable in an aqueous solution, but it is converted into the DTPA complex in the presence of excess DTPA. The cerium(III) complex produced by the reduction of the $^{144}Ce(IV)$-DTPA complex is not adsorbed on the cation exchange resin above pH 6, though an abrupt increase in the adsorption coefficient is observed below pH 6, indicating that the formation constant of Ce(III)Z is not very large.

## Discussion

Unusual chemical behavior of $^{144}Pr$ decayed from $^{144}Ce$ was observed more remarkably in the DTPA complex system than in the EDTA complex system. These results indicate that the chemical behavior of $^{144}Pr$ in the DTPA complex system cannot be explained sufficiently by the deactivation process proposed in the EDTA complex system.[1]

In order to treat the chemical behavior of $^{144}Pr$ more strictly, let us re-examine the assumption proposed in the EDTA complex system.

a) **Life Time of the $^{144}Pr(IV)$-DTPA Complex.** The cerium(IV)-DTPA complex is fairly stable compared to the cerium (IV)-EDTA com-

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[4] L. Eyring, H. Lohr and B. B. Cunningham, *J. Am. Chem. Soc.*, **74**, 1186 (1952).

plex.[5] Although the praseodymium(IV)-DTPA complex must be reduced to a tripositive state because of its thermodynamical instability, it may have a finite life time, with several possibilities.

**b) Decomposition Processes of $^{144}$Pr(III)Z.** Cerium(III)Z is stable in the aqueous solution, but its stability constant may be fairly small compared to the corresponding DTPA complex. The trace amount of $^{144}$Pr(III)Z, therefore, apparently decompose when a large excess of the DTPA complex is present.

**c) Adsorbability of $^{144}$Pr(III)Z on the Cation Exchange Resin.** The $^{144}$Pr(III)Z which may be produced by an intramolecular electron-transfer of the $^{144}$Pr(IV)-DTPA complex still has a negative charge. Consequently, it will not be adsorbed on the resin.

**d) Chemical Behavior of $^{144}$Pr Decayed from $^{144}$Ce$^{3+}$.** $^{144}$Pr will be reduced instantaneously to a tripositive state and exhibits the normal substitution reaction described above.

In view of these considerations, the introduction of Bateman's equation[6] has been undertaken in order to establish rigidly the stabilization process for the $^{144}$Pr decayed from $^{144}$Ce. The chain mechanism for the stabilization of $^{144}$Pr can be expressed as follows:

$$\begin{tikzcd}
{}^{144}\mathrm{Ce}^{3+} \arrow[r, "\lambda_{Ce}"] \arrow[dd, "\frac{\lambda_{Ce}N_1^\circ}{\lambda_{CeY}}"] & {}^{144}\mathrm{Pr}^{3+} \arrow[r, "\lambda_{PrY}"] \arrow[d, "\lambda_{Pr}"] & {}^{144}\mathrm{PrY}^{2-} \arrow[d, "\lambda_{Pr}"] & & \text{(Path I)} \\
 & \underline{\lambda_{Pr}N_2} & \underline{\lambda_{Pr}N_3} & & \\
{}^{144}\mathrm{CeY}^{2-} \arrow[r, "(1-\alpha)\lambda_{Ce}"] \arrow[dd, dash] & {}^{144}\mathrm{Pr(III)Z} \arrow[r, "\lambda_d"] \arrow[d, "\lambda_{Pr}"] & {}^{144}\mathrm{Pr}^{3+} \arrow[r, "\lambda_{PrY}"] \arrow[d, "\lambda_{Pr}"] & {}^{144}\mathrm{PrY}^{2-} \arrow[d, "\lambda_{Pr}"] & \\
 & \underline{\lambda_{Pr}N_4} & \underline{\lambda_{Pr}N_5} & \underline{\lambda_{Pr}N_6} & \text{(Path II)} \\
{} \arrow[r, "\alpha\lambda_{Ce}"] & {}^{144}\mathrm{Pr}^{3+} \arrow[r, "\lambda_{PrY}"] \arrow[d, "\lambda_{Pr}"] & {}^{144}\mathrm{PrY}^{2-} \arrow[d, "\lambda_{Pr}"] & & \text{(Path III)} \\
 & \underline{\lambda_{Pr}N_7} & \underline{\lambda_{Pr}N_8} & &
\end{tikzcd}$$

(6)

where $\lambda_{Ce}$ and $\lambda_{Pr}$ are the decay constants of $^{144}$Ce and $^{144}$Pr respectively; $\lambda_{CeY}$ and $\lambda_{PrY}$ denote the respective exchange rate constants of $^{144}$Ce$^{3+}$ and $^{144}$Pr$^{3+}$ with the cerium(III)-DTPA complex; $\lambda_d$, is the decomposition rate constant of an intermediate complex, and $\alpha$ is the ratio of bond-rupture, which is defined as the ratio of the $^{144}$Pr$^{3+}$ produced directly from the $^{144}$Ce(III)-DTPA complex without any formation of the intermediate.

Since the system considered here possesses a radiochemical equilibrium on the whole, the disintegration rate of $^{144}$Ce, $\lambda_{Ce}N$-, is equal to the sum of the disintegration rates of the respective fractions of $^{144}$Pr, *i. e.*, to $\sum_{n=2}^{8} \lambda_{Pr}N_n$. For the sake of simplicity, it is assumed that in the introduction of the chain mechanism, the tetrapositive praseodymium produced by the $\beta^-$-decay is promptly reduced to a tripositive state, and that the intermediate is not transferred to the cationic fraction upon separation. In Eq. (6), therefore, only the $\lambda_{Pr}N_3$, $\lambda_{Pr}N_4$, $\lambda_{Pr}N_6$, and $\lambda_{Pr}N_8$ fractions give any yield of $^{144}$PrY$^{2-}$. Thus, the solutions of Bateman's equation can be obtained for each fraction as follows:

i) The substitution reaction of the $^{144}$Pr$^{3+}$ initially present with the cerium(III)-DTPA complex gives the $^{144}$PrY$^{2-}$. After a lapse of time, *t*, the fraction of $^{144}$PrY$^{2-}$ is given by the following equation:

$$(\lambda_{Pr}N_3)_{I} = \lambda_{Ce}N_1^\circ\left(e^{-\lambda_{Pr}t} - e^{-(\lambda_{Pr}+\lambda_{PrY})t}\right)\frac{[^{144}\mathrm{PrY}^{2-}]_e}{[^{144}\mathrm{Pr}^{3+}]_e + [^{144}\mathrm{PrY}^{2-}]_e} \tag{7}$$

ii) Fraction of the formation of $^{144}$PrY$^{2-}$ by path I:

$$\begin{aligned}(\lambda_{Pr}N_3)_{II} = \lambda_{Ce}N_1^\circ\left(\frac{\lambda_{Pr}}{\lambda_{Pr}+\lambda_{PrY}-\lambda_{CeY}}\right)&\left\{e^{-(\lambda_{Pr}+\lambda_{PrY})t} + \frac{\lambda_{PrY}e^{-\lambda_{CeY}t}}{\lambda_{Pr}-\lambda_{CeY}}\right.\\ &\left.-\left(\frac{\lambda_{Pr}+\lambda_{PrY}-\lambda_{CeY}}{\lambda_{Pr}-\lambda_{CeY}}\right)e^{-\lambda_{Pr}t}\right\}\frac{[\mathrm{CeY}^{2-}]}{[\mathrm{Ce}^{3+}]+[\mathrm{CeY}^{2-}]}\cdot\frac{[^{144}\mathrm{PrY}^{2-}]_e}{[^{144}\mathrm{Pr}^{3+}]_e + [^{144}\mathrm{PrY}^{2-}]_e}\end{aligned} \tag{8}$$

iii) When $^{144}$Ce has reached the chemical equilibrium, it exists in the uncomplexed-ion form in the ratio of $[\mathrm{Ce}^{3+}]/\{[\mathrm{Ce}^{3+}]+[\mathrm{CeY}^{2-}]\}$. Consequently, it is necessary to obtain the fraction of the formation of $^{144}$PrY$^{2-}$ from $^{144}$Ce$^{3+}$ in path I without regard to the branches to path II and path III.

$$\begin{aligned}(\lambda_{PI}N_3)_{III} = \lambda_{Ce}N_1^\circ\left(\frac{\lambda_{PrY}}{\lambda_{Pr}+\lambda_{PrY}}\right)&\left\{1+\frac{\lambda_{Pr}}{\lambda_{PrY}}e^{-(\lambda_{Pr}+\lambda_{PrY})t}\right.\\ &\left.-\left(\frac{\lambda_{Pr}+\lambda_{PrY}}{\lambda_{PrY}}\right)e^{-\lambda_{Pr}t}\right\}\frac{[\mathrm{Ce}^{3+}]}{[\mathrm{Ce}^{3+}]+[\mathrm{CeY}^{2-}]}\cdot\frac{[^{144}\mathrm{PrY}^{2-}]_e}{[^{144}\mathrm{Pr}^{3+}]_e + [^{144}\mathrm{PrY}^{2-}]_e}\end{aligned} \tag{9}$$

iv) Contribution of the intermediate complex:

$$\lambda_{Pr}N_4 = (1-a)\lambda_{Ce}N_1^\circ\left\{\frac{\lambda_{Pr}}{\lambda_{Pr}+\lambda_d} - \frac{\lambda_{Pr}\,e^{-\lambda_{CeY}t}}{\lambda_{Pr}+\lambda_d-\lambda_{CeY}} - \frac{\lambda_{Pr}\lambda_{CeY}\,e^{-(\lambda_{Pr}+\lambda_d)t}}{(\lambda_{Pr}+\lambda_d)(\lambda_{CeY}-\lambda_{Pr}-\lambda_d)}\right\}\frac{[\mathrm{CeY}^{2-}]}{[\mathrm{Ce}^{3+}]+[\mathrm{CeY}^{2-}]} \tag{10}$$

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[5] T. R. Bhat and D. Radhamma, *Indian J. Chem.*, **3**, 151 (1965).

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

v) The degree of formation of $^{144}PrY^{2-}$ by path II:

$$\lambda_{Pr}N_6 = (1-a)\lambda_{Ce}N_1^{\circ}\Big\{\frac{\lambda_{PrY}\lambda_d}{(\lambda_{Pr}+\lambda_{PrY})(\lambda_{Pr}+\lambda_d)} - \frac{\lambda_{Pr}\lambda_{PrY}\lambda_d e^{-\lambda_{CeY}t}}{(\lambda_{Pr}-\lambda_{CeY})(\lambda_{Pr}+\lambda_d-\lambda_{CeY})(\lambda_{Pr}+\lambda_{PrY}-\lambda_{CeY})}$$
$$+ \frac{\lambda_{Pr}\lambda_{PrY}\lambda_{CeY} e^{-(\lambda_{Pr}+\lambda_d)t}}{(\lambda_{Pr}+\lambda_d)(\lambda_{PrY}-\lambda_d)(\lambda_{CeY}-\lambda_{Pr}-\lambda_d)} - \frac{\lambda_{CeY}e^{-\lambda_{Pr}t}}{\lambda_{CeY}-\lambda_{Pr}} + \frac{\lambda_{Pr}\lambda_{CeY}\lambda_d e^{-(\lambda_{Pr}+\lambda_{PrY})t}}{(\lambda_{Pr}+\lambda_{PrY})(\lambda_d-\lambda_{PrY})(\lambda_{CeY}-\lambda_{Pr}-\lambda_{PrY})}\Big\}$$
$$\times \frac{[CeY^{2-}]}{[Ce^{3+}]+[CeY^{2-}]}\cdot\frac{[^{144}PrY^{2-}]_e}{[^{144}Pr^{3+}]_e+[^{144}PrY^{2-}]_e} \tag{11}$$

vi) The degree of formation of $^{144}PrY^{2-}$ by path III:

$$\lambda_{Pr}N_8 = \alpha\lambda_{Ce}N_1^{\circ}\Big\{\frac{\lambda_{PrY}}{\lambda_{Pr}+\lambda_{PrY}} - \frac{\lambda_{Pr}\lambda_{PrY} e^{-\lambda_{CeY}t}}{(\lambda_{Pr}+\lambda_{PrY}-\lambda_{CeY})(\lambda_{Pr}-\lambda_{CeY})}$$
$$+ \frac{\lambda_{Pr}\lambda_{CeY} e^{-(\lambda_{Pr}+\lambda_{PrY})t}}{\lambda_{CeY}-\lambda_{Pr}-\lambda_{PrY})(\lambda_{Pr}+\lambda_{PrY})} - \frac{\lambda_{CeY}e^{-\lambda_{Pr}t}}{\lambda_{CeY}-\lambda_{Pr}}\Big\}\frac{[CeY^{2-}]}{[Ce^{3+}]+[CeY^{2-}]}\cdot\frac{^{144}PrY^{2-}]_e}{[^{144}Pr^{3+}]_e+[^{144}PrY^{2-}]_e} \tag{12}$$

In deriving these equations, $\lambda_{Ce}$ is very small compared to $\lambda_{Pr}$, $\lambda_{CeY}$, $\lambda_{PrY}$, and $\lambda_d$, and could be considered to be effectively zero. After a sufficient lapse of time, when a chemical equlibrium with respect to $^{144}Ce$ has been attained and when the $^{144}Pr^{3+}$ initially present has decayed out, only the iii, iv, v, and vi fractions contribute to the $^{144}PrY^{2-}$- yield. In addition, the exponential terms in all the equations become, in effective, zero; hence, the $^{144}PrY^{2-}$-yield is given by the following equation:

$$^{144}PrY^{2-}\text{-yield}(\%) = \Big\{\frac{\lambda_{PrY}}{\lambda_{Pr}+\lambda_{PrY}}\cdot\frac{[Ce^{3+}]+a[CeY^{2-}]}{[Ce^{3+}]+[CeY^{2-}]}\cdot\frac{[^{144}PrY^{2-}]_e}{[^{144}Pr^{3+}]_e+[^{144}PrY^{2-}]_e}$$
$$+\frac{(1-a)\lambda_{Pr}}{\lambda_{Pr}+\lambda_d}\cdot\frac{[CeY^{2-}]}{[Ce^{3+}]+[CeY^{2-}]}+\frac{(1-a)\lambda_{PrY}\lambda_d}{(\lambda_{Pr}+\lambda_{PrY})(\lambda_{Pr}+\lambda_d)}$$
$$\times\frac{[CeY^{2-}]}{[Ce^{3+}]+[CeY^{2-}]}\cdot\frac{[^{144}PrY^{2-}]_e}{[^{144}Pr^{3+}]_e+[^{144}PrY^{2-}]_e}\Big\}\times 100 \tag{13}$$

where the effect of the disintegration of $^{144}Ce$ can be ignored; by convention, the value for $\lambda_{Ce}N_1^{\circ}$ is taken as unity. Thus, the $^{144}PrY^{2-}$-yield becomes a constant, independent of the reaction time.

In Eq. (13), since the values for $\lambda_{Pr}$ and $\lambda_{PrY}$ have already been established, $\lambda_d$ and $\alpha$ can be obtained by insertion of the experimental values for the $^{144}PrY^{2-}$-yields. It was found that $\alpha$ is a constant independent of the temperature, while $\lambda_d$ is a function of the concentration of hydrogen ion; that is,

$$\lambda_d = k_d[H^+] \tag{14}$$

The values for the decomposition rate constants of the intermediate, $k_d$, and for $\alpha$ obtained which best fit the experimental results are given below:

(25°C) $k_d = (5\pm1)\times10^4\ l\,mol^{-1}min^{-1}$
( 5°C) $k_d = (2\pm1)\times10^4\ l\,mol^{-1}min^{-1}$
$\alpha = 0.25$

The experimental and calculated values for the $^{144}PrY^{2-}$-yields are compared in Fig. 3, using the following numerical values:

$\lambda_{Pr} = 0.0396$, $\lambda_d = 10^{4.7}[H^+]$, $\alpha = 0.25$ and
$\lambda_{PrY} = \{10^{8.90}[CeY^{2-}]/[Ce^{3+}]+10^{8.36}\}[H^+]^2$

The values for $(1-F)$ in Eq. (5) were also calculated with Eqs. (7)—(12), as shown in Fig. 6. The good agreement between the experimental and calculated values for the $^{144}PrY^{2-}$-yields supports the proposed decomposition process of the intermediate complex, which is substantially analogous to that proposed in the EDTA complex system.[1)]

The theoretical considerations of the $\beta^-$-decay, in addition to the results of the charge spectrometric studies, would predict that a large fraction of the transformation of a $\beta$-active atom in a molecule would leave the daughter molecular ion in a little-excited or not in an excited state at all. Furthermore, in the $\beta^-$-decay of $^{144}Ce$, multiple charging resulting from electron shake-off and the internal conversion of $\gamma$-rays is of minor importance, and the maximum amount of internal energy

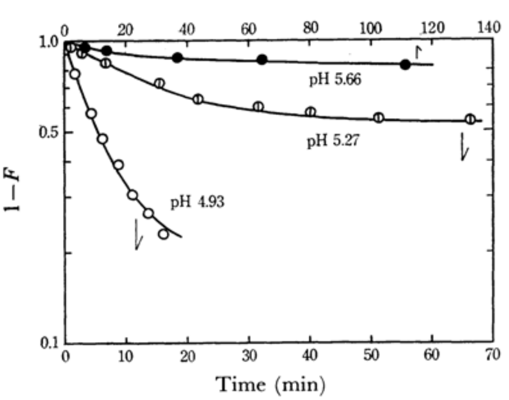

Fig. 6. The $(1-F)$ values calculated by Eqs. (7)—(12).
The circles indicate the experimental values.
The solid curves were calculated by Eqs. (7)—(12).

available from the recoil is less than the bond energies. Thus, the chemical properties of the daughter molecular ion ($^{144}$Pr(IV)-DTPA complex) play the most important role in determining the fate of the $^{144}$Pr decayed from the $\beta^-$-decay of $^{144}$Ce.

Glentworth *et al.*[2] have reported that an attack of the hydrogen ion on the charged excited intermediate molecules ($[^{144}\text{Pr}^{\text{IV}}\text{Y}]^{\neq}$) produced by $\beta^-$-decay results in an enhanced break-up of the daughter complex ion. However, by taking into consideration the facts that the praseodymium(IV) ion is a very powerful oxidizing agent and that inversely, aminopolycarboxylic acids are reducing agents, it is more likely that, before the attack of the hydrogen ion on the $^{144}$Pr(IV)-DTPA complex, a unimolecular decomposition resulting from an intramolecular electron-transfer takes place predominantly. Evidence for the reduction by the intramolecular electron-transfer has been found in the cerium(IV)-DTPA complex.

In view of the decomposition mechanism and rate canstants, there is no doubt that the intermediate complex is present. The intramolecular electron-transfer would cause the decarboxylation of a coordinated carboxylate group, and the resultant intermediate complex is possibly less stable than the corresponding parent complex. The value for the rate constant, $k_d$, is consistent with these considerations.

The multiple charging of the daughter ion resulting from electron shake-off and the internal conversion of $\gamma$-rays is of minor importance in the $\beta^-$-decay of $^{144}$Ce, but it cannot be ignored completely.[7] About 18 per cent of $^{144}$Pr possesses a charge higher than $+5$ resulting from the electron shake-off, judging from the results in the $\beta^-$-decay of $^{133}$Xe.[8] Furthermore, the yield of 13 per cent for the multiply-charged species is estimated from the internal conversion coefficient.[9] Consequently, a considerable part of $^{144}$Pr might be found in the multiply-charged state, while in about 70 per cent of the events the daughter would be formed in an oxidation state one higher than its parent in the $\beta^-$-decay of $^{144}$Ce. Multiple charging may cause an exhaustive decomposition of the daughter complex, resulting in the liberation of $^{144}$Pr in the free-ion form. Indeed, the ratio of the bond rupture of 0.25 corresponds to the extent of the formation of the multiply-charged $^{144}$Pr ion.

In addition, in higher pH regions the degree of bond-rupture should give plateau values for the $^{144}\text{PrY}^{2-}$-yield curves indepedent of the temperature. As is shown in Fig. 4, both the $^{144}\text{PrY}^{2-}$-yields at 25 and 5°C seem to reach the plateau value of 37.5 per cent with an increase in the pH; however, as a result of the hydrolysis of the uncomplexed cerium(III) ion, further investigation could not be carried out.

In conclusion, these considerations lead to a possible stabilization process for the $^{144}$Pr decayed from $^{144}$Ce, as is illustrated schematically in Fig. 7.

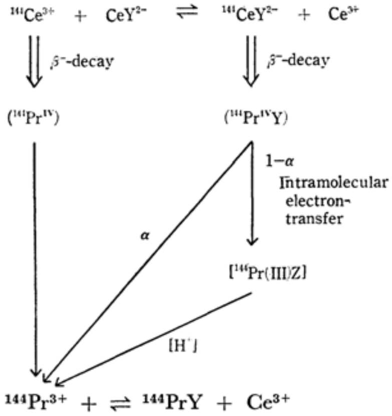

Fig. 7. Stabilization processes of $^{144}$Pr produced by $\beta^-$-decay of $^{144}$Ce in the DTPA complex system.

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[7] T. Shiokawa, H. Kudo and T. Omori, This Bulletin, **42**, 436 (1969).

[8] A. H. Snell and F. Pleasonton, *Phys. Rev.*, **111**, 1338 (1958).

[9] I. Pullman and P. Axel, *ibid.*, **102**, 1366 (1956).