Anal Calcd for $C_{22}H_{22}N_4O_2$: C, 70.56; H, 5.92; N, 14.96; O, 8.55. Found: C, 70.01; H, 5.98; N, 15.04; O, 8.71.

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Formation and Dissociation Kinetics of Tetraaza-Crown-Alkanoic Acid Complexes of Cerium(III)

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The formation and dissociation rates of Ce^{3+} Complexes of the 1,4,7,10-tetraaza-13,16-dioxacyclooctadecane-N,N', N'',N'''-tetraacetic acid (**1**), 1,4,7,10-tetraaza-13,16-dioxacyclooctadecane-N,N',N'',N'''-tetramethylacetic acid (**2**), and 1,4,7,10-tetraaza-13,16-dioxacyclooctadecane-N,N',N'',N'''-tetrapropionic acid (**3**) have been measured by the use of stopped-flow spectrophotometry. Observations were made at 25.0 ± 0.1 °C and at an ionic strength of 0.10 M $NaClO_4$. The complexation of Ce^{3+} ion with **1** and **2** proceeds through the formation of an intermediate complex $(CeH_3L^{2+})^*$ in which the Ce^{3+} ion is incompletely coordinated. This may then lead to be a final product in the rate-determining step. Between pH 4.76 and 5.76, the diprotonated (H_2L^{2-}) from is revealed to be a kinetically active species despite of its low concentration. The stability constants $(\log K_{(CeH_3L2+)^*})$ and specific water-assisted rate constants (k_{OH}) of intermediate complexes have been determined from the kinetic data. The dissociation reactions of Ce^{3+} complexes of **1**, **2**, and **3** were investigated with Cu^{2+} ions as a scavenger in acetate buffer. All complexes exhibit acid-independent and acid-catalyzed contributions. The effect of buffer and Cu^{2+} concentration on the dissociation rate has also been investigated. The ligand effect on the dissociation rate of Ce^{3+} complexes is discussed in terms of the side-pendant arms and the chelate ring sizes of the ligands.

Introduction

In recent years, there has been growing interest in the ma-

crocyclic receptors containing in their framework both oxygen and nitrogen atoms.[1,2] The molecular recognition and activation of anionic or neutral substrates has led to a further development in the chemistry of such macrocycles.[3,4] Several factors influence the kinetics of formation and dis-

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sociation of lanthanide complexes of macrocyclic polyaza-polycarboxylates, including charge density, ring size, number of donor atoms, and ring and side arm substituents.[5-9] Recently studies on the lanthanide complexes of polyoxa- and polyazapolycarboxylates demonstrated the dependence of the formation and dissociation rates on the basicity of the nitrogen atoms and the rigidity of the ligands.[10-13] Sherry *et al.* reported the formation and dissociation rates of Gd^{3+} complexes of $DETA^{3-}$, $MeDETA^{3-}$, and Me_2DETA^{3-} ($DETA^{3-}$ =1,4,7-triazacyclodecane-N,N',N''-triacetate).[14] The formation kinetic data of these complexes conformed to the rapid formation of an intermediate, which converted to the final complex. The dissociation rates of these complexes were dependent on the substitution of the methyl groups on a ring carbon of the ligands. We have recently studied the stability and kinetics of some metals with macrocyclic receptors, N-pendant arms N_3O_2 (1,4,10-triaza-7,13-dioxacyclopentadecane)[15-17] and N_3O_3 (1,7,13-triaza-4,10,16-trioxacyclooctadecane).[18] In these studies, the metal complexes of these macrocycles lead to the decrease in thermodynamic and kinetic stabilities compared with the saturated polyazapolycarboxylate ligands.

The objective of this work is to determine the formation and dissociation rates of Ce^{3+} complexes with macrocyclic tetraazadioxa ligands with acetate, methylacetate, and propionate groups as N-pendent arms (Figure 1). We intend to investigate the effect of donor atoms, chelate ring size and N-pendent arms of macrocyclic ligands on the kinetic properties of these complexes.

Experimentals

Synthesis of Ligands. 1,4,7,10-tetraaza-13,16-diox-acyclooctadecane tetrahydrobromide was prepared by the previous procedures.[19,20] Ligands, 1,4,7,10-tetraaza-13,16-dioxacyclooctadecane-N,N',N'',N'''-tetraacetic acid (**1**), 1,4,7,10-tetraaza-13,16-dioxacyclooctadecane-N,N',N'',N'''-tetramethylacetic acid (**2**), and 1,4,7,10-tetraaza-13,16-diox-acyclooctadecane-N,N',N'',N'''-tetrapropionic acid (**3**), were synthesized according to the method of Martell *et al.*[21] The ligands were characterized by ^1H NMR and elemental analysis. **1**: ^1H NMR (D_2O-NaOD, pD 13.2): 3.60 (s, 4H, -OCH_2CH_2O-), 3.35 (t, 4H, -OCH_2CH_2N-), 2.82 (t, 4H, -OCH_2CH_2N), 2.54 (s, 12H, -NCH_2CH_2N-), 2.32 (s, 8H, -NCH_2COOH). Anal. Cacld for $C_{20}H_{40}N_4O_2$: C, 65.18; H,
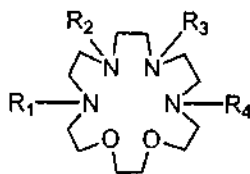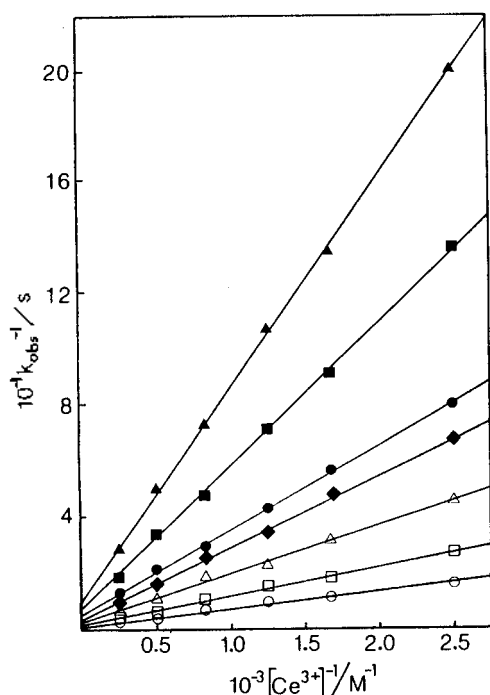
10.94; N, 15.20. Found: C, 65.42, H, 10.58; N, 15.55. **2**: ^1H NMR (D_2O-NaOD, pD 13.2): 3.57 (s, 4H, -OCH_2CH_2O-), 3.38 (t, 4H, -OCH_2CH_2N-), 2.73 (t, 4H, -OCH_2CH_2N), 2.64 (s, 12H, -NCH_2CH_2N-), 2.20 (q, 4H, -$NCH(CH_3)COOH$), 1.52 (d, 12H, -$NCH(CH_3)COOH$). Anal. Cacld for $C_{24}H_{48}N_4O_2$: C, 67.88; H, 11.39; N, 13.19. Found: C, 68.11, H, 11.28; N, 13.24. **3**: ^1H NMR (D_2O-NaOD, pD 13.2): 3.65 (s, 4H, -OCH_2CH_2O-), 3.25 (t, 4H, -OCH_2CH_2N-), 2.78 (t, 4H, -OCH_2CH_2N), 2.53 (s, 12H, -NCH_2CH_2N-), 2.60 (t, 4H, -NCH_2CH_2COOH), 2.10 (t, 12H, -NCH_2CH_2COOH). Anal. Cacld for $C_{24}H_{48}N_4O_2$: C, 67.88; H, 11.39; N, 13.19. Found: C, 67.91, H, 11.98; N, 13.10.

Preparation of Solutions. A stock solution of Ce^{3+} was prepared from $CeCl_3$ (Aldrich, 99.9%) and its concentration was determined by complexometric titration using xylenol orange as indicator. The concentrations of the ligand stock solution were determined by titration against a standardized $Cu(ClO_4)_2$ solution using murexide as an indicator. Sodium perchlorate was used to control the ionic strength in all kinetic studies. All solutions were made in deionized water. All other chemicals were reagent grade and were used without further purification.

Measurements. The ionic strength was adjusted to 0.10 M with $NaClO_4$. A Beckman model $\Phi71$ pH meter with a combination electrode was used for all pH measurements. The H^+ ion concentration was established from the measured pH value by procedures reported previously.[22] Kinetic measurements were carried out using a Hi-Tech stopped-flow spectrophotometer interfaced with a scientific data acquisition system. The temperature of the reaction was maintained at 25.0 ± 0.1 °C with the use of a Lauda RM6 circulatory water bath. The sample solutions of formation reaction were buffered with 1.0×10^{-2} M sodium acetate/acetic acid. The formation rates of Ce(L) were measured by following the change in absorbance of Ce(L) at 270 nm, where the absorbance of uncomplexed Ce^{3+} is not significant. The concentration of the ligands was 2.0×10^{-4} M, while that of Ce^{3+} was varied between 4.0×10^{-4} and 4.0×10^{-3} M. The dissociation rates of Ce(L) were studied in acidic solutions in the presence of excess Cu^{2+} ions. Under these conditions, the dissociation reaction takes place and the progress of the exchange may be monitored by the formation of Cu(L) at 285 nm. The concentration of Ce(L) was 5.0×10^{-5} M, while that of the Cu^{2+} ion was varied between 2.0×10^{-4} and 1.0×10^{-3} M. The buffer solutions were made by varying the ratio of concentration of acetic acid and sodium acetate necessary for attainment of the desired pH.

Results and Discussion

Formation Kinetics. The formation rates of the complexes were studied at different pH values as a function of excess [Ce^{3+}] to ensure first-order kinetics. At a given pH 4.76-5.76, the measured k_{obs} (pseudo-first-order rate constant) values increased with increasing [Ce^{3+}] and plots of k_{obs} versus [Ce^{3+}] show saturation behavior. This is characteristic of rapid formation of the intermediate complex that rearranges to the final product in a rate-determining step. The dependence of k_{obs} values on [Ce^{3+}] can be expresses as[23]

1. $R_1 = R_2 = R_3 = R_4 = CH_2COOH$

2. $R_1 = R_2 = R_3 = R_4 = CHCOOH$
              CH_3

3. $R_1 = R_2 = R_3 = R_4 = CH_2CH_2COOH$

Figure 1. Structure of the tetraaza-crown-alkanoic acids.

Figure 2. Plots of k_{obs}^{-1} vs. $[Ce^{3+}]^{-1}$ for the formation kinetics of Ce(2) at different pH values. [2]=2.0×10⁻⁴ M; [OAc⁻]=0.01 M; T=25.0±0.1 °C; I=0.10 M (NaClO₄); pH=4.78 (○), 4.91 (□), 5.10 (△), 5.23 (◆), 5.39 (●), 5.55 (■), 5.75(▲).
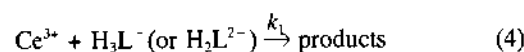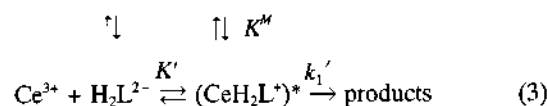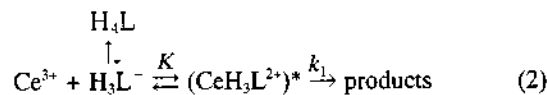
$$k_{obs} = \frac{k_1 K[Ce^{3+}]}{1+K[Ce^{3+}]} \tag{1}$$

where K is the equilibrium constant for the formation of the intermediate complex and k_1 is the rate constant for the rearrangement of the intermediate to the final product. Plots of $1/k_{obs}$ against $1/[Ce^{3+}]$ lead to straight lines as shown in Figure 2. The values of k_1, K and the second-order rate constant $k_2=k_1K$ were obtained from Eq. (1) and are summarized in Table 1. The protonated forms of 1 and 2 could

Table 1. Rate data for Ce³⁺ complex formation with 1 and 2 at 25.0±0.1 °C, I=0.10 M (NaClO₄), and [OAc⁻]=1.0×10⁻² M

Lig-ands	pH	$k_1(s^{-1})$	$K(M^{-1})$	$k_2(M^{-1}s^{-1})$
	4.76	5.66±0.13	(6.20±0.16)× 10¹	(3.51±0.12)× 10²
	4.90	6.63±0.08	(7.62±0.11)× 10¹	(5.05±0.10)× 10²
	5.09	8.20±0.14	(7.41±0.18)× 10¹	(6.07±0.18)× 10²
1	5.21	9.37±0.18	(9.03±0.22)× 10¹	(8.46±0.26)× 10²
	5.36	11.8±0.05	(12.2±0.08)× 10¹	(14.4±0.11)× 10²
	5.55	16.6±0.17	(11.9±0.21)× 10¹	(19.9±0.41)× 10²
	5.76	23.9±0.33	(13.8±0.38)× 10¹	(32.9±1.01)× 10²
	4.78	(1.11±0.04)× 10⁻¹	(1.19±0.06)× 10²	(1.32±0.08)× 10¹
	4.91	(1.31±0.08)× 10⁻¹	(1.50±0.09)× 10²	(1.96±0.17)× 10¹
	5.10	(1.55±0.10)× 10⁻¹	(2.19±0.11)× 10²	(3.40±0.28)× 10¹
2	5.23	(1.92±0.06)× 10⁻¹	(2.11±0.08)× 10²	(4.04±0.20)× 10¹
	5.39	(2.69±0.12)× 10⁻¹	(2.18±0.13)× 10²	(5.87±0.44)× 10¹
	5.55	(3.51±0.08)× 10⁻¹	(2.82±0.09)× 10²	(9.87±0.39)× 10¹
	5.75	(5.26±0.16)× 10⁻¹	(3.13±0.18)× 10²	(16.5±1.07)× 10¹

contribute to the complexation kinetics of Ce³⁺ ion between pH 4.76 and 5.76. The concentrations of protonated ligands were computed with the use of ligand protonation constants.[24] In this pH range H_3L is major species (60.44-93.43%), H_4L is an important contributor (38.59-5.89%), and H_2L^{2-} represents 0.043-0.68% of the total ligand concentration. On the basis of these results, the formation reaction of Ce³⁺ complexes may be expressed by Eqs. (2)-(4).

$$H_4L$$
$$\uparrow\!\!\!\!\downarrow$$
$$Ce^{3+} + H_3L^- \underset{K}{\rightleftharpoons} (CeH_3L^{2+})^* \xrightarrow{k_1} products \tag{2}$$

$$\uparrow\!\!\!\!\downarrow \qquad \uparrow\!\!\!\!\downarrow K^M$$

$$Ce^{3+} + H_2L^{2-} \underset{K'}{\rightleftharpoons} (CeH_2L^+)^* \xrightarrow{k_1'} products \tag{3}$$

$$Ce^{3+} + H_3L^- (or\ H_2L^{2-}) \xrightarrow{k_1''} products \tag{4}$$

The stability constants of the intermediates $(CeH_3L^{2+})^*$ can be obtained from K values at a given pH, using known protonation constants of the ligands by Eq. (5).

$$K_{(CeH_3L^{2+})}^* = K(1+K_4[H^+]+K_4K_5[H^+]^2) \tag{5}$$

The calculated stability constants of the intermediate complexes summarized in Table 2. The stability constants of the intermediates obtained here are about one order of magnitude higher than those for the corresponding monoacetate and monomethylacetate complexes.[26] This suggests that the Ce³⁺ ion is coordinated to more than one carboxylate oxygen in the intermediate. A similar result also observed for the formation of Ln(N₃O₂Ac) (1,4,10-triaza-7,13-dioxacyclo-pentadecane-N,N',N"-triacetic acid).[15] The stability constant for the intermediate of Ce(2) is somewhat larger than that of Ce(1). This fact may be attributed to the thermodynamic stability ($\log\beta_{Ce(1)}$=15.06 versus $\log\beta_{Ce(2)}$=16.00).[27] From the kinetic data, the second-order rate constant k_{HnL} also represents $(k_1K)_{HnL}$. If one species is markedly more reactive than all the others, the second-order rate constant could be obtained from the following expression[28]

$$k_2=k_{HnL}(1+K_{H(n+1)L}^{-1}[H^+])^{-1} \tag{6}$$

where $K_{H(n+1)L}$ is the protonation constants of 1 and 2. From the plots of k_2 against $(1+K_{H(n+1)L}^{-1}[H^+])^{-1}$, the second-order rate constants for the H_2L^{2-} and H_3L^- species are collected in Table 2. Despite of their very low concentration in the pH range observed, the H_2L^{2-} species appears to be kinetically much more reactive than the H_3L^- species, even though the latter is the major component in solution. The low reactivity of the H_3L^- form may be assigned to the for-

Table 2. Stability constants ($\log K_{(CeH_3L_2+)}$), second-order rate constants (k_{HnL}), and water-assisted rate constants (k_{OH}) of the intermediate complexes at 25.0±0.1 °C and I=0.10 M (NaClO₄)

Comp-lexes	$\log K_{(CeH_3L_2+)}$	$k_{H_2L^{2-}}$ (M⁻¹s⁻¹)	$k_{H_3L^-}$ (M⁻¹s⁻¹)	k_{OH} (M⁻¹s⁻¹)
Ce(1)	2.08±0.07	6.36±0.21 ×10⁶	4.86±0.16 ×10⁵	2.71±0.05 ×10⁹
Ce(2)	2.54±0.04	(5.17±0.16) ×10⁵	(4.32±0.14) ×10⁴	(6.41±0.12) ×10⁷

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mation of trizwitterionic form of 1 and 2. The three N-H⁺ groups in the 18-membered cycle of H₃L⁻ probably hinder the rearrangement of the intermediate complex into the final chelate product due to the electrostatic repulsion with the incoming Ce³⁺ ion. The same conclusion was reported previously by Kasprzyk and Wilkins.[29]

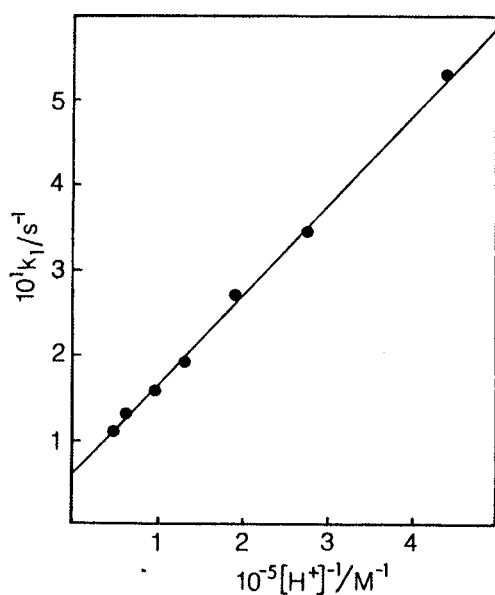The values of k_1 were increased with increasing pH (Table 1) and followed Eq. (7).[10]

$$k_1 = k_{H_2O} + k_{OH} K_w [H^+]^{-1} \qquad (7)$$

This relationship was explained in terms of a water-assisted reorganization of the intermediate $(CeH_2L^+)^*$. According to Eq. (7) a plot of k_1 vs $[H^+]^{-1}$ is expected to be a straight line as shown in Figure 3. This observation is consistent with the previously reported works.[10,15,16,18] The k_{OH} values calculated from the slope of the straight line in Figure 3 and Eq. (7) ($\log K_w = 13.78$) are listed in Table 2. A significant contribution from the base form of the buffer is not expected, since the concentration of buffer used in the present work is low. The k_{OH} value of Ce(2) is about two orders of magnitude smaller than that of Ce(1). This indicates that the substitution of three methyl groups on the acetate pendant arms of 1 makes the ligand more rigid.[14]
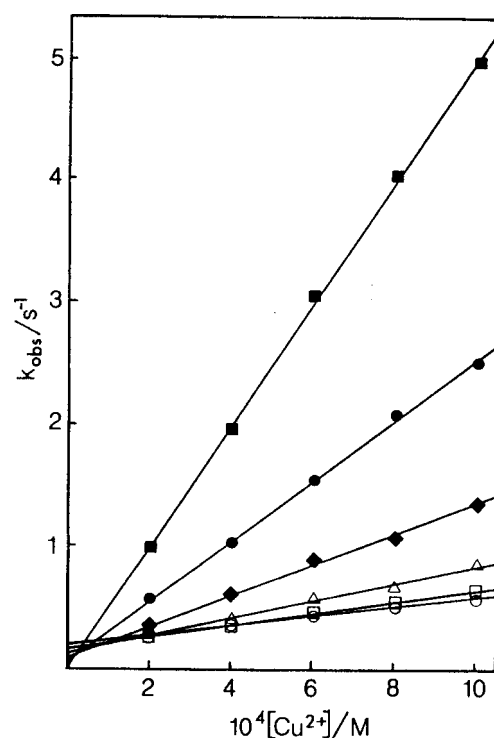
Dissociation Kinetics. Since the stability constants of Cu²⁺ complexes are much greater than those of Ce³⁺ complexes,[27] the exchange reaction is complete in the presence of excess Cu²⁺ ions

$$Ce(L) + Cu^{2+} \longrightarrow Cu(L) + Ce^{3+} \qquad (8)$$
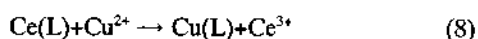
where L is the H₃L⁻ form under the pH range 4.37-5.58. The experimental data show excellent pseudo-first-order reaction rates. The observed rate constants kobs were found to be independent of [OAc⁻] but dependent on [Cu²⁺]. The dependence of k_{obs} on [Cu²⁺] is plotted in Figure 4 at different pH values. In each case, the data fit straight lines with measurable non-zero intercepts, which confirm the exchange reaction as proceeding via both [Cu²⁺]-independent

Figure 4. Plots of k_{obs} vs. [Cu²⁺] for the dissociation kinetics of Ce(3) at different pH values. [Ce(3)]=5.0×10⁻⁵ M; [OAc⁻]=0.01 M; T=25.0±0.1 °C; I=0.10 M (NaClO₄); pH=4.37 (○), 4.59 (□), 4.77 (△), 4.97 (◆), 5.28 (●), 5.58 (■).

and [Cu²⁺]-dependent pathways. The observed k_{obsd} (pseudo-first-order rate constants) can therefore be expressed as

$$k_{obsd} = k_d + k_{Cu} [Cu^{2+}] \qquad (9)$$

where k_d and k_{Cu} are the functions of acidity, [H⁺]. Figure 5 shows that k_d is proportional to [H⁺], while k_{Cu} is pro-

Figure 3. Plots of k_1 vs. $[H^+]^{-1}$ for the formation kinetics of Ce (2) at 25.0±0.1 °C and I=0.10 M (NaClO₄).
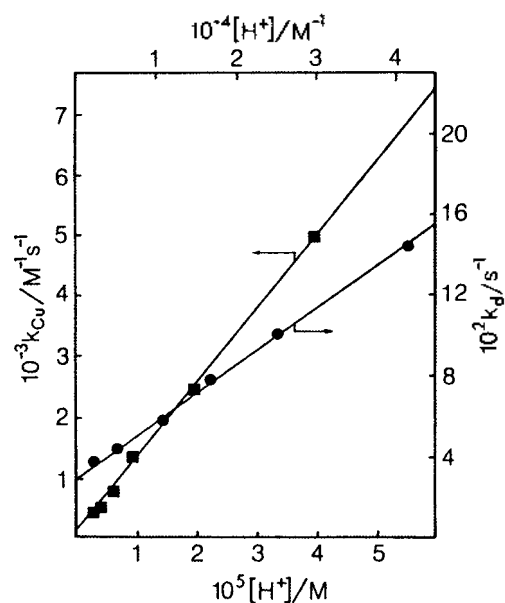

Figure 5. Plots of k_d vs. [H⁺] and k_{Cu} vs. $[H^+]^{-1}$ for the dissociation kinetics of Ce(3). [Ce(3)]=5.0×10⁻⁵ M; [OAc⁻]=0.01 M; T=25.0±0.1 °C; I=0.10 M (NaClO₄).

Table 3. Rate constants for the dissociation reactions of Ce^{3+} complexes of macrocyclic ligands at 25.0 ± 0.1 °C and I=0.10 M ($NaClO_4$)

Complexes	k_d (s^{-1})	k_H (M^{-1}s^{-1})	k_{Cu} (M^{-1}s^{-1})	k_{CuOH^+} (M^{-1}s^{-1})
Ce(1)	$(1.10\pm0.08)\times10^{-2}$	$1.52\pm0.06)\times10^{3}$	$1.33\pm0.33)\times10^{1}$	$(1.12\pm0.07)\times10^{4}$
Ce(2)	$(4.88\pm0.42)\times10^{-4}$	$(7.05\pm0.18)\times10^{2}$	7.00 ± 0.38	$(5.27\pm0.15)\times10^{3}$
Ce(3)	$(3.08\pm0.08)\times10^{-2}$	$(2.08\pm0.08)\times10^{3}$	$(7.87\pm0.39)\times10^{2}$	$(8.18\pm0.08)\times10^{5}$
Ce(N$_3$O$_3$Ac)^a	$(1.60\pm0.05)\times10^{-1}$	$(1.12\pm0.04)\times10^{4}$	$(7.43\pm0.11)\times10^{3}$	$(2.71\pm0.05)\times10^{7}$

^{a} Reference 18.

portional to $[H^+]^{-1}$. On the basis of these results, the overall rate of dissociation reaction can be expressed as

$$\text{Rate}=k_d[Ce(L)]+k_H[Ce(L)][H^+]+k_{Cu}[Ce(L)][Cu^{2+}]$$
$$+k_{CuH-1}[Ce(L)][Cu^{2+}][H^+]^{-1} \qquad (10)$$

The rate constants (k_d, k_H, k_{Cu}, and k_{CuH-1}) calculated from the experimental data are presented in Table 3. The reaction between Ce^{3+} complexes and Cu^{2+} ion proceeds by reaction pathways that are similar to those reported for the exchange of Ce^{3+} ion in their macrocyclic polyoxa- and polyaza-carboxylate complexes.[7,15,18] As can be seen, the first and second terms in Eq. (10) are responsible for the dissociative pathway of the Cu^{2+}-independent mode. The rate-determining step involves the loss of Ce^{3+} ion from the complexes and the rapid reaction of the released ligand with Cu^{2+} ion. Eq. (10) also represents the associative pathway of the Cu^{2+}-dependent mode, which is composed of the direct attack of the Cu^{2+} ion on partially dissociated Ce-L and the $[H^+]^{-1}$ dependence. $[H^+]^{-1}$ behavior can be interpreted by the existence of the attack of hydrolyzed copper species ($CuOH^+$) on Ce-L, even though the investigated pH is not higher. k_{CuOH^+} is therefore calculated by the expression

$$k_{CuH-1}=k_{CuOH^+}\beta_{CuOH^+} \qquad (11)$$

where β_{CuOH^+} ($=K_{CuOH^+}K_w$) is a stability constant (*i.e.* 2.0×10^{-8}).[30]

A comparison of the dissociation rate constants of Ce^{3+} complexes in Table 3 indicates that the rates of the dissociative pathway decrease in the order Ce(3) > Ce(1) > Ce(2). Both rate constants are significantly affected by the side arm substituents and chelate ring sizes of the ligands. The dissociation rate of Ce(1) complex was found to be faster than that of Ce(2) complex. This indicated that the substitution of four methyl groups on the acetate pendant arms of 1 increases the rigidity of the macrocycle, yielding a complex with even greater kinetic stability. A methyl substitution in other polyazapolycarboxylate ligands has also been observed to increase the inertness of their resulting complexes.[14] The rate constant of both the acid-independent and acid-catalyzed pathway of the Ce(3) complex is about one order of magnitude larger than that of the corresponding Ce(1). This fact may be attributed to the destabilizing effect of the six-membered N-Ce-O chelate ring involving the four propionate group of 3. A similar argument has been used to explain the fact that the dissociation rate of Eu (ENDPDA)$^-$ (ethylenedinitrilo- N,N'-di(3-propanoic)-N,N'-diacetic acid)[31] is much faster than that of Eu(EDTA)$^-$. The acid-catalyzed rate constant of Ce(1) is about one order of magnitude smaller than that of Ce(N$_3$O$_3$Ac) (1,7,13-triaza-4, 10,16-trioxacyclooctadecane-N,N',N''-triacetic acid),[18] even though 1 has the same cavity size (18-membered cycle) as

N$_3$O$_3$Ac. This may be due to the increase of thermodynamic stability ($\log\beta_{Ce(1)}=15.06$ versus $\log\beta_{Ce(N_3O_3Ac)}=14.15$),[27] the difference in the type of cyclic donor atoms, and the number of acetate pendant arms of ligands.

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Relaxation of Photogenerated Carriers under He, H$_2$, CO$_2$ and O$_2$ on ZnO

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The relaxation process of photogenerated carriers was investigated using conductivity measurement on ZnO under He, H$_2$, CO$_2$ and O$_2$. The process was well explained with the rate constant of reaction or recombination of hole and electron, k_h and k_e ($k_h > k_e$), respectively. Generally, k_h increased with the pressure of the gases. The slope of k_h with respect to the pressure increased in the order of H$_2$ $\leq$ He $<$ CO$_2$, while k_h of O$_2$ was sensitive to the history of the sample. The relaxation process on ZnO which was exposed to oxygen at 298 K and 573 K was observed during the illumination at 298 K and it was found that the rate constant of hole decreased with illumination time. From the result, it was suggested that the rate constant of photogenerated excess carriers was affected by the surface barrier of the semiconductor.

Introduction

Photocatalysis on solid surface is an important field in environmental science and surface photochemistry, and it involves absorption of photon by solid and admolecules accompanying a change of the population of electron in the energy levels of solid and admolecules, and electron transfer between them. When the solid is a semiconductor, the absorption of photon induces an excitation of electron from valence band to conduction band of the semiconductor and increases the number of electron and hole in the valence and the conduction bands, respectively. Then, the photogenerated excess carriers react with chemical species or recombination centers to release the photon energy. In the photocatalytic process, the reaction of minority carrier in the relaxation process is more important than that of majority carrier since the majority carrier can react with the chemical species even in the absence of photon. For example, photodecomposition of organic molecule on TiO$_2$ (n-type) is initiated by the reaction of photogenerated hole (minority carrier) with the molecule or with water molecule forming hydroxyl radical,[1,2] while electron (majority carrier) does not contribute to the reaction pathway of the photo-

catalytic reaction. Therefore it is necessary to understand the (reaction) rate constant of the minority carrier to improve the yield of photocatalytic reactions. In this paper, the rate constant of photogenerated hole was studied by means of the relaxation of photoconductivity on ZnO (n-type semiconductor) under several gases. The relations of the rate constant with the height of surface barrier, surface state concentration and cross-section of the adsorbed species were discussed.

Basic Concept

When we illuminate a semiconductor with photons having the energy greater than the band gap energy, electrons in valence band excite to conduction band and there is a deviation from the thermal equilibrium in the concentration of carriers. After blocking of the light, the photogenerated holes and electrons recombine with specific rates. We can trace the relaxation process from the decay of conductivity of semiconductor.

For the case of direct recombination of photocarriers, the photoconductivity, $\Delta\sigma$, can be written as

$$\Delta\sigma = Ae^{-kt} \tag{1}$$