Ligand-Substitution Reaction Kinetics of Tris(8-quinolinolato)- and Bis-(2-methyl-8-quinolinolato)(8-quinolinolato)aluminum(III) Complexes with Ethylenediamine-*N,N,N',N'*-tetraacetic Acid

Tomonori HORIHATA, Ken-ichi OKAMOTO,† Jinsai HIDAKA,† and Hisahiko EINAGA*
Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305
†Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305
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Synopsis. Ligand-substitution reactions of $[Al(hq)_3]$ and $[Al(hq)(mhq)_2]$ (H(m)hq: (2-methyl-)8-quinolinol) with H_4edta have been studied at 25 °C and 1.0 mol dm^{-3} NaCl by means of the stopped-flow spectrophotometric method. Three concurrent reaction pathways, a dissociative activation one and two parallel associative activation ones, to which H_2edta^{2-} and Hedta^{3-} contribute, are elucidated.

Only one ligand-substitution reaction kinetics of aluminum(III) chelate complexes with multidentate ligands has been studied,[1] although they are of fundamental importance in the elucidation of the kinetic characteristics of aluminum(III). In our previous paper,[1] a ligand-substitution reaction of an aluminum(III) complex containing 7-[(2-carboxyphenyl)-azo]-8-hydroxy-5-quinolinesulfonic acid (H_3pqs) with 8-hydroxy-5-quinolinesulfonic acid was studied; it was found that the reaction proceeds with dissociative activation and with the liberation of one of the pqs^{3-} in $[Al(pqs)_2]^{3-}$ as the rate-determining step. In a subsequent investigation of the ligand-substitution reactions of an aluminum(III) complex containing 8-quinolinol (Hhq) and one containing Hhq and 2-methyl-8-quinolinol (Hmhq) with ethylenediamine-*N,N,N',N'*-tetraacetic acid (H_4edta); it was found, besides the dissociative activation process, which has been accepted as a general kinetic feature of aluminum-(III) (vide infra), that there exist processes in which the coordinating ligand participates and that these processes take place concurrently. This paper will be concerned with the ligand-substitution reaction kinetics and mechanisms of $[Al(hq)_3]$ and $[Al(hq)(mhq)_2]$ with H_4edta.

Experimental

Complexes. $[A(hq)_3]\cdot 1/2H_2O$. This complex was prepared from stoichiometric mixtures of aluminum(III) and Hhq in an ethanolic aqueous solution of pH 5—6.[2] Found: C, 69.75; H, 4.05; N, 8.80%. Calcd for $C_{27}H_{19}N_3O_{3.5}Al$: C, 69.22; H, 4.08; N, 8.97%.

$[Al(hq)(mhq)_2]\cdot 1/2H_2O$. Hmhq (3.2g, 0.020 mol) in 200 cm^3 ethanol was added to $AlK(SO_4)_2\cdot 12H_2O$ (4.7 g, 0.010 mol) in 200 cm^3 of an aqueous solution below pH 4. To the solution we then added Hhq (1.5 g, 0.010 mol) in 100 cm^3 of ethanol, and the resulting solution was adjusted to pH 5—6 with aqueous NH_3 to obtain a crystalline precipitate. The complex was recrystallized from acetone and was dried in vacuo at 140 °C for 7 h. Found: C, 70.38; H, 4.11; N, 8.87%. Calcd for $C_{29}H_{23}N_3O_{3.5}Al$: C, 70.15; H, 4.66; N, 8.46%.

Measurements. Kinetic runs were carried out in an ethanolic aqueous solution (ethanol, 10 vol%) of 1.0 mol dm^{-3} NaCl at 25.0±0.2 °C on a JASCO stopped-flow spectrophotometer[3] under pseudo-first-order kinetic conditions with respect to the H_4edta concentration. The change in the absorbance with the time was followed at 260 nm, where the aluminum(III) complexes of the 8-quinolinolate-type ligands (10^{-5}—10^{-3} mol dm^{-3}, λ_{max}: ca. 252 nm) showed a maximum absorbance against the free ligand. The rate constant, k_{obsd}, was calculated from Eq. 1:

$$\ln (A_0 - A_\infty)/(A_t - A_\infty) = k_{obsd}\, t \qquad (1)$$

Here, A_0, A_t, and A_∞ stand for absorbances at the initial state, at time t, and at equilibrium respectively. The hydrogen-ion concentration was measured, in principle, according to the literature procedure.[3] Analysis by the curve-fitting method (vide infra) was carried out with an NEC PC-9801VM2 personal computer.

Results and Discussion

The ligand-substitution reaction kinetics of $[Al(hq)_n(mhq)_{3-n}]$ (n=1 and 3) with H_4edta proceed in weakly acidic aqueous media (pH 3.0—4.5), where H_4edta is present mainly in the species of H_3edta$^-$, H_2edta^{2-}, Hedta^{3-} and slightly in that of H_4edta.[4] The preliminary absorption spectral study gave evidence that $[Al(hq)_n(mhq)_{3-n}]$ turned quantitatively into $[Al(edta)]^-$ at equilibrium under the kinetic conditions specified in the experimental section. The dependence of the absorbance at a specified wavelength on the time

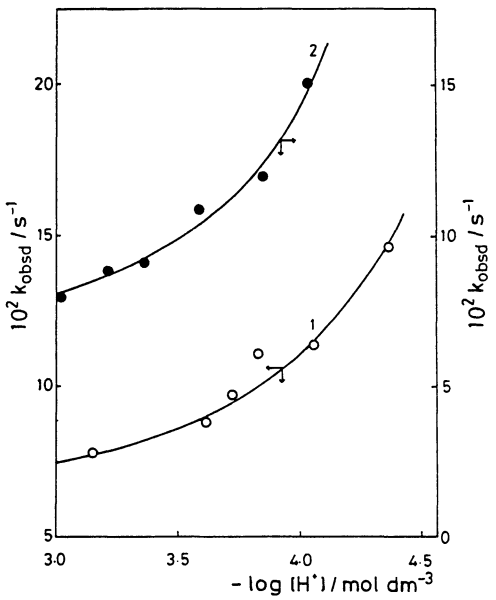

Fig. 1. Relation between k_{obsd} and $-\log[H^+]$. 1: $[Al(hq)_3]$, 1.49×10^{-5} mol dm^{-3}; and C_{edta}, 3.79×10^{-3} mol dm^{-3}. 2: $[Al(hq)(mhq)_2]$, 1.53×10^{-5} mol dm^{-3}; and C_{edta}, 3.78×10^{-3} mol dm^{-3}. 1.0 mol dm^{-3} NaCl (ethanol, 10 vol%), 25 °C.

conformed well to Eq. 1 for more than three half-life periods under a constant total H_4edta concentration, C_{edta}, and hydrogen-ion concentration, $-\log[H^+]$; this fact indicates that there is only one rate-determining step in the ligand-substitution reaction. The experimental data obtained under pseudo-first-order kinetic conditions with respect to C_{edta} are shown in Figs. 1 and 2. These data indicate that k_{obsd} depends not only on $-\log[H^+]$ but also on C_{edta}; k_{obsd} increases exponentially with the increases in $-\log[H^+]$ and in $\log C_{edta}$. The dependence of k_{obsd} on C_{edta} implies that H_4edta contributes to the ligand-substitution reaction. Hence, the rate equation can be given as follows (cf. Appendix):

$$-d[[Al(hq)_n(mhq)_{3-n}]]/dt = k_{obsd}[[Al(hq)_n(mhq)_{3-n}]]$$
$$k_{obsd} = \{k_d + [f_2([H^+]) + f_4([H^+])]C_{edta}/f_1([H^+])\}/[1 + f_3([H^+])]C_{edta}/f_1([H^+]) \quad (2)$$

Equation 2 indicates that the k_{obsd} vs. C_{edta} curve at a constant $-\log[H^+]$ should be asymptotic to a limiting line of:

$$k_{obsd,\infty} = [f_2([H^+]) + f_4([H^+])]/f_3([H^+]) \quad (2')$$

with an increase in C_{edta}. This is not the case for the present investigation, as is evident from Fig. 2 for $[Al(hq)_3]$. Therefore, the contribution of the $f_3([H^+])$ and $f_4([H^+])$ terms in Eq. 2 should be negligible; any possibilities can be excluded of the k_{osj} process and hence of any contribution of a mechanism in which a coordinated ligand is replaced by an entering ligand in the outer-sphere complex as the mechanistic rate-determining step. Accordingly, Eq. 2 can be simplified as follows:

$$k_{obsd} = k_d + [f_2([H^+])/f_1([H^+])]C_{edta} \quad (3)$$

It is reasonable to assume that the presence of H_4edta species and the contribution of the k_{i_4} pathway to the kinetics can be neglected above $-\log[H^+]$ of 3 (vide infra). Therefore, Eq. 3 can be modified to Eq. 4:

$$k_{obsd} = k_d + k_{i3}C_{edta} + \{(k_{i2} - k_{i3})K_{a2}[H^+] + (k_{i1} - k_{i3})\}C_{edta}/(K_{a3}K_{a2}[H^+]^2 + K_{a2}[H^+] + 1) \quad (4)$$

Equation 4 can be analyzed for the k_{obsd} vs. $-\log[H^+]$ relation by means of the curve-fitting method[5] with a normalized curve of:

$$Y = (av + b)/((K_{a3}/K_{a2})v^2 + v + 1\} + c,\ X = -\log v \quad (5)$$

with $a \equiv (k_{i2} - k_{i3})C_{edta}$, $b \equiv (k_{i1} - k_{i3})C_{edta}$, and $c \equiv k_d + k_{i3}C_{edta}$. Likewise, Eq. 4 can be analyzed for the k_{obsd} vs. $\log C_{edta}$ relation with a normalized curve of:

$$Y' = a'u + c',\ X' = \log u \quad (6)$$

with $a' \equiv f_2([H^+])/f_1([H^+])$ and $c' \equiv k_d$. Hence, the k_{ij}'s and k_d can be estimated from the a, b, c, and c' constants and the experimental parameter of C_{edta}. These rate constants can then be refined by using the a' constant, the K_{aj}'s, and the experimental parameter of $-\log[H^+]$. The k_{obsd} vs. $-\log[H^+]$ and the k_{obsd} vs. $\log C_{edta}$ relations in Figs. 1 and 2 were used for the analysis; the rate constants thus estimated are summarized in Table 1. The k_{i_3} rate constant was found to be negligibly smaller than k_d, which indicates that the k_{i_3} pathway, like the k_{i_4} one, does not contribute to the ligand-substitution processes. Hence, the substitution reaction of $[Al(hq)_n(mhq)_{3-n}]$ with H_4edta is concluded to proceed through the k_d and the k_{ij} (j: 1 and 2) pathways, to the latter of which H_2edta^{2-} and $Hedta^{3-}$ contribute, as the rate-determining steps.

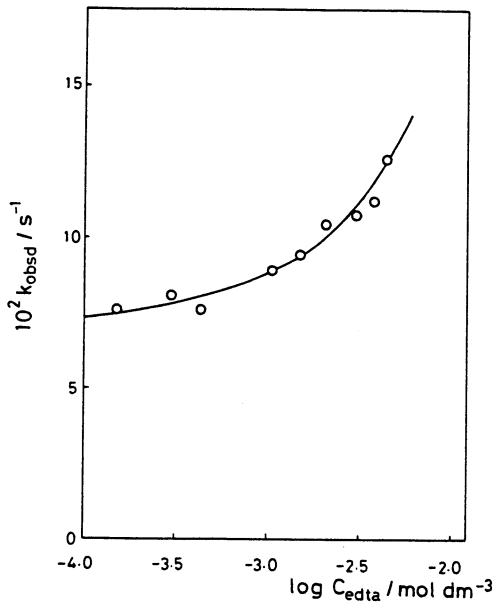

Fig. 2. Relation between k_{obsd} and $\log C_{edta}$. $[Al(hq)_3]$, 1.49×10^{-5} mol dm^{-3}; and $-\log[H^+]$, 3.83. 1.0 mol dm^{-3} NaCl (ethanol, 10 vol%), 25 °C.

It was found in the present investigation that the ligand-substitution reaction of $[Al(hq)_n(mhq)_{3-n}]$ with H_4edta proceeds through three reaction pathways, irrespective of the composition of the starting complex. The rate constants decrease in the following order: $k_{i1} > k_{i2} > k_d$ ($k_{i3} \fallingdotseq k_{i4} \fallingdotseq 0$). Each rate constant differs slightly with different compositions of the complex. Therefore, we would like to focus our attention first on the reaction kinetics of $[Al(hq)_3]$.

The dissociative activation pathway (k_d) of $[Al(hq)_3]$ is considered to originate from the nature of the aluminum(III) of an octahedral coordination.[6] In fact, the k_d of 7×10^{-2} s^{-1} of $[Al(hq)_3]$ is in fairly good agreement with that of 3×10^{-2} s^{-1} of $[Al(pqs)_2]^{3-}$,[1] when differen-

Table 1. Rate Constants for the Ligand-Substitution Reactions

Complex	k_d/s^{-1}	k_{i2}/mol^{-1} dm^3 s^{-1}	k_{i1}/mol^{-1} dm^3 s^{-1}	Remarks
$[Al(hq)_3]$	$(7.3\pm0.5)\times10^{-2}$	3.6±0.2	$(1.30\pm0.05)\times10^3$	This work[a]
$[Al(hq)(mhq)_2]$	$(7.5\pm0.5)\times10^{-2}$	4.0±0.2	$(2.38\pm0.05)\times10^3$	This work[a]
$[Al(pqs)_2]^{3-}$	$(3.00\pm0.43)\times10^{-2}$	—	—	Ref. No. 1[b]

a) 1.0 mol dm^{-3} NaCl (ethanol, 10 vol%), 25 °C. b) 0.1 mol dm^{-3} NaCl, 25 °C.

ces in the configuration and the chelate-ring structure of these two complexes are taken into consideration. The dissociative activation pathway may be initiated by a cleavage of the metal-oxygen bond of the coordinated quinolinolato ligand, for the Al-O bond of $[Al(hq)_3]$ has been estimated, by the ^1H NMR spectral[7] and the magnetic circular dichroism spectral[8] studies, to be dominantly ionic and highly labile.

There are two parallel associative activation pathways (k_{i1} and k_{i2}) in competition with the dissociative activation one (k_d). The k_{i1} rate constant, to which $Hedta^{3-}$ relates, is about three orders of magnitude larger than the k_{i2} rate constant, to which H_2edta^{2-} relates. This difference in the rate constants can not be ascribed simply to formation of the outer-sphere complex with the entering ligand by ionic or related interaction, because $[Al(hq)_3]$ has no formal charge and because no experimental evidence on the formation of the outer-sphere complex was obtained; the difference can, however, be ascribed to numbers of the protons blocking the coordination sites of the entering ligand.

Two associative activation mechanisms, the associative (A) and the associative interchange (I_a), can possibly explain the k_{i1} and k_{i2} pathways. However, the I_a mechanism may be more probable than the A one in view of the facts that aluminum(III) of a small ionic radius prefers intrinsically to take the dissociative interchange (I_d) mechanism[1,9] and that the k_{i1} and k_{i2} pathways do not become appreciable until the concentration of the entering ligand reaches a high point compared with that of the starting complex. These reaction pathways may be initiated by the substitutional interchange of the coordinated bulky quinolinolato ligand with the glycinate ligating group of H_4edta, probably to form an intermediate of the $[Al(hq)_2(Hedta\text{-}O,N)]^{2-}$ type.

No appreciable differences were noticed in the rate constants of $[Al(hq)_3]$ and $[Al(hq)(mhq)_2]$. These two ligands may take an equal opportunity to leave in the first step.

Appendix

The following general expression of k_{obsd} can be derived from the text:

$$k_{obsd} = \frac{k_d + \sum_{j=1}^{4} k_{ij}[H_j\,edta^{(4-j)-}] + \sum_{j=1}^{4} k_{osj}\,K_{osj}[H_j\,edta^{(4-j)-}]}{1+\sum_{j=1}^{4} K_{osj}[H_j\,edta^{(4-j)-}]}. \quad (A1)$$

Here, k_d, k_{ij}, and k_{osj} are the rate constants for the dissociative activation, the associative activation, and the outer-sphere complex related reaction processes, while K_{osj} is the formation constant for the outer-sphere complex. Equation A1 can, by using C_{edta} ($=\sum_{j=1}^{4}[H_jedta^{(4-j)-}]$), be rearranged to Eq. 2 with:

$$f_1([H^+]) \equiv (K_{a4}K_{a3}K_{a2}[H^+]^3 + K_{a3}K_{a2}[H^+]^2 + K_{a2}[H^+] + 1)K_{a1}[H^+], \quad (A2)$$

$$f_2([H^+]) \equiv (k_{i4}K_{a4}K_{a3}K_{a2}[H^+]^3 + k_{i3}K_{a3}K_{a2}[H^+]^2 + k_{i2}K_{a2}[H^+] + k_{i1})K_{a1}[H^+], \quad (A3)$$

$$f_3([H^+]) \equiv (K_{os4}K_{a4}K_{a3}K_{a2}[H^+]^3 + K_{os3}K_{a3}K_{a2}[H^+]^2 + K_{os2}K_{a2}[H^+] + K_{os1})K_{a1}[H^+], \quad (A4)$$

$$f_4([H^+]) \equiv (k_{os4}K_{os4}K_{a4}K_{a3}K_{a2}[H^+]^3 + k_{os3}K_{os3}K_{a3}K_{a2}[H^+]^2 + k_{os2}K_{os2}K_{a2}[H^+] + k_{os1}K_{os1})K_{a1}[H^+], \quad (A5)$$

where the K_{aj}'s are the protonation constants of H_4edta ($K_{aj}=[H_jedta^{(4-j)-}]/[H^+][H_{j-1}edta^{(5-j)-}]$, j: 1—4).[4]

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4) The following data were used as the K_{aj} values of H_4edta at 25 °C and the ionic strength of 0.1 mol dm^{-3} (A. E. Martell and R. M. Smith, "Critical Stability Constants," Plenum, New York (1974), Vol. 1, p. 204): $\log K_{a1}=10.17$, $\log K_{a2}=6.11$, $\log K_{a3}=2.68$, and $\log K_{a4}=2.0$, because only small changes in magnitude are expected as a result of the differences in the ionic strength of 0.1 and 1.0 mol dm^{-3} (cf. L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Chem. Soc., London(1971), Sp. Pub. No. 25, p. 63).

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9) It has been widely accepted that aluminum(III) proceeds through the I_d mechanism, although it is difficult to exclude totally the possibility of the (limiting) dissociative (D) mechanism. See, for example, a) A. E. Merbach, *Pure Appl. Chem.*, **54**, 1479 (1982); b) D. Fiat and R. E. Connick, *J. Am. Chem. Soc.*, **90**, 608 (1968); c) L. S. Frankel and E. P. Danielson, *Inorg. Chem.*, **11**, 1964 (1972); d) C. Ammann, P. Moore, and A. E. Merbach, *Helv. Chim. Acta*, **63**, 268(1980); e) D. Hugi-Cleary, L. Helm, and A. E. Merbach, *Helv. Chim. Acta*, **68**, 545 (1985).