

Bound-Ligand Effect in the Complexation Kinetics of Hydroxozirconium(IV) and Hydroxohafnium(IV) Complexes

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The kinetics of the complexation reaction of zirconium(IV) and hafnium(IV) with Semixylenol Orange (H_4L) have been studied spectrophotometrically by means of a stopped-flow technique. The rate of formation of the complex is expressed as $d[MHL^+]/dt = k_1[M^{4+}][H_3L^+][H^+]^{-2} + k_2[M^{4+}][H_3L^+][H^+]^{-3} - k_3[MHL^+][H^+] - k_4[MHL^+][H^+]^2$ for both metal ions (M^{4+}). With values of k_1 and k_2 , assuming a dissociative interchange mechanism for the first two reaction paths in this rate equation, the rate constants of the loss of coordinated water molecules at MOH^{3+} and $M(OH)_2^{2+}$ were estimated. With these rate constants, the γ parameters for both metal ions, which describe the acceleration effect of the bound ligand A ($A=OH^-$ in this study) on the water exchange rate at MA, were also estimated. With the same parameter, some possibilities to design a new kinetic-catalytic method of analysis based on ligand-substitution reactions involving zirconium(IV) were proposed.

Keywords Zirconium, hafnium, Semixylenol Orange, complexation kinetics, bound ligand effect

Ligand-substitution reactions of a metal-chromogenic ligand complex (MR) with a polycarboxylic or aminopolycarboxylic type of multidentate ligand (Y) is written as (charges are omitted for simplicity)



where k_f is the overall forward rate constant. This reaction system has been widely used in inorganic differential kinetic analysis.¹⁻⁴ In some of these reactions, it has been found that the reactions are catalytically accelerated by an additional ligand, and that this catalytic effect provides a basis for a kinetic determination of the ligand carrying such a catalytic feature.^{5,6} For example, the ligand-substitution reaction of mercury(II)-4-(2-pyridylazo)resorcinol (PAR) complex with 1,2-cyclohexanediamine-*N,N,N',N'*-tetraacetic acid (CDTA) is accelerated by halide ions, and, based on the difference in the catalytic effect, a kinetic method for determining iodide as low as 10^{-8} M has been proposed in the presence of bromide and chloride in large excess.⁵

From a mechanistic consideration concerning the formation constant of a mixed-ligand complex MAL, it has been proposed^{7,8} that the relative (to water) rate constant for the dissociation of the ligand (L) from a complex (MAL), $(k_{MAL}^{-L}/k_M^{-H_2O})$, can be expressed as

$$\log(k_{MAL}^{-L}/k_M^{-H_2O}) = \gamma E(A) - \alpha E(L) - \beta H(L). \quad (2)$$

E and H refer to the electron-donor constant and basicity constant of the specified ligand, respectively; their values

which are normalized to zero for water, have been given for typical monodentate ligands⁹ and some selected multidentate ligands.¹⁰ α , β , and γ are constants characteristic of the metal ion (M). Their values were estimated from the stability of the metal complex⁹ and the reactivity of the metal ion and its complex.^{11,12}

Mechanistic studies concerning the reaction system (1) reveal, in most cases, that the reaction proceeds *via* a rapid formation of an intermediate (RMY) followed by dissociation of R from RMY as a rate-determining step. For this reaction scheme, k_f is expressed as¹³

$$k_f = K_{RMY}^Y k_{RMY}^{-R} = K_{os(MR,Y)} \times (k_{MR}^{-H_2O}/k_{RMY}^{-Y}) \times k_{RMY}^{-Y}, \quad (3)$$

where $K_{RMY}^Y = [RMY]/([MR][Y])$ and $K_{os(MR,Y)}$ is the formation constant of the outersphere complex formed between MR and Y. From Eqs. (2) and (3), the following expression is derived for $\log k_f$:

$$\log k_f = \log K_{os(MR,Y)} + \alpha\{E(Y) - E(R)\} + \beta\{H(Y) - H(R)\} + \gamma E(Y) + \log k_M^{-H_2O}. \quad (4)$$

When the third ligand (A) is present in reaction system (1) as a catalyst, an additional reaction path involving an intermediate RAMY appears, and the overall forward rate constant for this catalytic path (k_f^\wedge) is expressed as

$$k_f^\wedge = K_{MAR}^A \times K_{RMY}^Y \times k_{RMY}^{-R}. \quad (5)$$

In the same fashion as in $\log k_f$, the following expression is derived for $\log k_f^\wedge$

$$\log k_f^A = \log K_{os(MA,R)} + \log K_{os(MAR,Y)} + \alpha\{E(A) + E(Y) - E(R)\} + \beta\{H(A) + H(Y) - H(R)\} + \gamma\{E(A) + E(Y)\} + \log k_M^{-H_2O} \quad (6)$$

Combining Eqs. (4) and (6), we have

$$\log(k_f^A/k_f) = \log\{K_{os(MA,R)}K_{os(MAR,Y)}/K_{os(MR,Y)}\} + \alpha E(A) + \beta H(A) + \gamma E(A) \quad (7)$$

When the same charge is assumed for A, the first term in the right-hand side of Eq. (7) is constant for a given combination of M, R and Y. Furthermore, the contribution of this term is not so large compared to the others. We thus obtain

$$\log(k_f^A/k_f) = \alpha E(A) + \beta H(A) + \gamma E(A) \quad (8)$$

Upon substituting the relationship¹⁴ $\log K_{MA} - \log K_{os(M,A)} = \alpha E(A) + \beta H(A)$ into Eq. (8), we obtain

$$\log(k_f^A/k_f) = \log K_{MA} - \log K_{os(M,A)} + \gamma E(A) \quad (9)$$

With these equations and the parameters α , β , γ , E , and H , the acceleration effect of halide ions on the ligand-substitution reaction of mercury(II)-PAR complex with CDTA are quantitatively described;¹³ for $M = \text{Hg}^{2+}$, which is a typical soft metal ion and has negligibly small γ value, iodide, a softer ligand than bromide or chloride, makes the value of $\log K_{MA}$ larger, and, thus, accelerates the reaction more extensively.

When hard metal ions, such as Zr^{4+} and Hf^{4+} , are employed as M in the presence of a hard ligand (A) as a catalyst in reaction system (1), a significant acceleration effect of A can be anticipated, due to large value of $\log K_{MA}$ in Eq. (9). Unfortunately, the values of γ for these metal ions have not yet been obtained. This impedes any quantitative prediction of the catalytic effect based on the approach described above. Thus, making use of hydroxide as A, we studied the complexation kinetics of hydroxozirconium(IV) and hydroxohafnium(IV) with Semixylenol Orange (Fig. 1), and estimated the values of γ for Zr^{4+} and Hf^{4+} .

Experimental

Reagents

Semixylenol Orange (SXO, H_4L) was synthesized by Mannich condensation^{15,16}, and purified by cellulose column chromatography.¹⁷ *Anal.* Calcd. for $\text{C}_{26}\text{H}_{25}\text{NO}_9\text{S} \cdot 3\text{H}_2\text{O} \cdot 0.85\text{HCl}$: C, 51.0; H, 5.1; N, 2.3; Cl, 4.9; Found: C, 50.8; H, 4.7; N, 2.4; Cl, 4.8%. The purity of SXO was checked by a spectrophotometric molar-ratio method using complexation with Cu^{2+} at pH 4.85, and was found to be 99.7%. A zirconium solution was prepared by fusing the oxide (Nakarai, 99.9%) with sodium hydrogensulfate, leaching the cooled melt with water, precipitating the hydroxide with ammonia, washing the precipitate with water, and finally dissolving

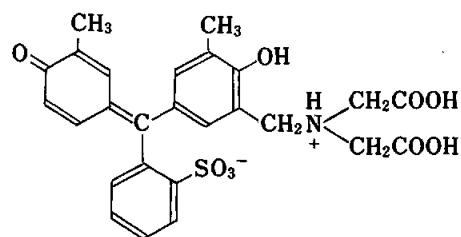


Fig. 1 Structure of Semixylenol Orange (SXO, H_4L).

the hydroxide with perchloric acid. The content of zirconium and perchloric acid in the stock solution was determined by chelatometry and alkalimetry to be 1.03×10^{-3} M and 11.8 M, respectively. Hafnium solution was prepared with the oxide (Raremetallic, 99.95%) and standardized by the same procedure as mentioned above. The stock solution contained 1.04×10^{-3} M Hf(IV) and 11.8 M perchloric acid.

Apparatus

The absorption spectra and absorbance were measured with a Hitachi Model 124 and 139 spectrophotometers, respectively. The reaction rates were followed by a stopped-flow analyzer (Model RA 401, Otsuka Electronics), equipped with a data processor (Model RA 451). The changes in the absorbance at 535 nm, the wavelength of maximum absorption by the 1 : 1 complex, were accumulated to obtain high S/N curves. The temperature of the reaction solution was controlled to $25.0 \pm 0.1^\circ\text{C}$. The ionic strength (I) was maintained at 3 M with sodium perchlorate. The acidity in the reaction solution was adjusted with perchloric acid.

Results and Discussion

Protonation equilibrium of SXO

Over the $-\log[\text{H}^+]$ range from -0.5 to 2.0 the spectra of SXO changed with a distinct isosbestic point at 475 nm. This spectral change is attributable to the protonation of H_4L ,¹⁵

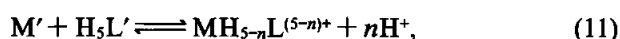


Analyzing the absorbance changes at 450 and 515 nm, the wavelengths of maximum absorption by H_4L and H_5L^+ , respectively, as a function of $[\text{H}^+]$, $K_{\text{H}_5\text{L}^+} = [\text{H}_5\text{L}^+]/([\text{H}_4\text{L}][\text{H}^+])$ at 25°C and $I=3$ M (Na,H)ClO₄ was determined to be $10^{9.24 \pm 0.01}$ by a least-squares curve-fitting method.

Complexation equilibria of Zr(IV) and Hf(IV) with SXO

At $[\text{H}^+]=0.2$ M, a molar-ratio method at 535 nm proved that each metal ion gives a 1 : 1 SXO complex. Then, under conditions where the total concentration of the metal ion (C_M) is in excess over that of SXO (C_L) and the metal ion is present solely as a monomeric species^{18,19},

the complexation equilibrium of M^{4+} with SXO can be expressed as



where

$$\begin{aligned} [M'] &= [M^{4+}] + [MOH^{3+}] + [M(OH)_2^{2+}] \\ &= [M^{4+}](1 + \beta_1[H^+]^{-1} + \beta_2[H^+]^{-2}) \\ &= [M^{4+}]\alpha_{M(OH)} \end{aligned} \quad (12)$$

$$\begin{aligned} [H_5L'] &= [H_5L^+] + [H_4L] \\ &= [H_5L^+](1 + K_{H_5L}^{-1}[H^+]^{-1}) \\ &= [H_5L^+]\alpha_{H_5L(H)}. \end{aligned} \quad (13)$$

Here, β_i is the overall hydrolysis constant of M^{4+} . The conditional equilibrium constant (K') for reaction (11) is correlated with $K = ([MH_{5-n}L^{(5-n)+}][H^+]^n) / ([M^{4+}][H_5L^+])$ as

$$\begin{aligned} K' &= ([MH_{5-n}L^{(5-n)+}][H^+]^n) / ([M'] [H_5L']) \\ &= K / (\alpha_{M(OH)}\alpha_{H_5L(H)}). \end{aligned} \quad (14)$$

The concentration of the respective species involved in Eq. (14) at a given $[H^+]$ is expressed as a function of the absorbance (A) to be

$$[MH_{5-n}L^{(5-n)+}] = (A - A_1)C_L / (A_2 - A_1), \quad (15)$$

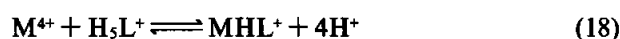
$$[H_5L'] = (A_2 - A)C_L / (A_2 - A_1) \quad (16)$$

and

$$[M'] = C_M - (A - A_1)C_L / (A_2 - A_1), \quad (17)$$

respectively. A_1 and A_2 refer to the absorbance of the reaction solution when the equilibrium (11) is shifted quantitatively to the left and right, respectively. The value of A_1 was determined by measuring the absorbance of SXO in the absence of $M(IV)$ with silica cuvettes (light path: 1 cm). Thus, by rearranging Eq. (14), the plot of $\log([MH_{5-n}L^{(5-n)+}] / [H_5L'])$ against $\log[M']$ gives a straight line with a slope of unity and an intercept (I) of $\log K - \log(\alpha_{M(OH)}\alpha_{H_5L(H)}) - n \times \log[H^+]$.

The absorbance changes at 535 nm were analyzed as a function of C_M to find A_2 by a least-squares method. The values of the molar absorption coefficient (ϵ) which gave the best-fit curves were 8.27×10^4 and $8.11 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ for the zirconium and the hafnium complexes, respectively. Then, $I + \log(\alpha_{M(OH)}\alpha_{H_5L(H)})$ obtained at various $[H^+]$ were plotted against $-\log[H^+]$ to determine n and $\log K$. The plots for zirconium and hafnium gave straight lines with slopes (n) of 3.8 ± 0.2 and 3.9 ± 0.1 , respectively. Thus, the complexation of M^{4+} with H_5L^+ can be expressed as



with $\log K = 5.24 \pm 0.03$ and 4.43 ± 0.03 for the zirconium and the hafnium complexes, respectively. The solid lines in Fig. 2 are the best-fit curves calculated with the obtained parameters. Higher formation constant for

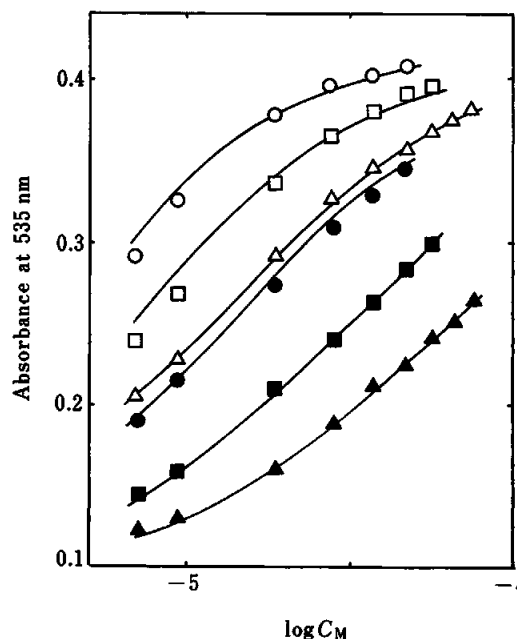
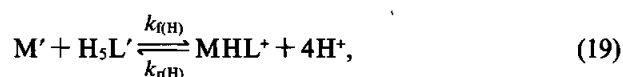


Fig. 2 Plot of absorbance at 535 nm against $\log C_M$. Conditions: $C_{SXO} = 5.02 \times 10^{-6} \text{ M}$; $[H^+]/M$: 0.6 (○, ●), 0.8 (□, ■), 1.0 (△, ▲); the open and filled symbols are for Zr(IV) and Hf(IV), respectively. All at 25°C and $I = 3 \text{ M}$.

the zirconium complex is consistent with its higher value⁹ of α for zirconium, as compared to that for hafnium.

Complexation kinetics of Zr(IV) and Hf(IV) with SXO

As found from equilibrium studies, zirconium and hafnium ions form a 1 : 1 complex with SXO in acidic solution in which the concentration of the metal ion is in large excess over that of the ligand:



where $k_{f(H)}$ and $k_{r(H)}$ are conditional rate constants involving the concentration of hydrogen ion for the forward and reverse reactions, respectively. Then, the kinetic equation for this reaction is expressed as

$$d[MHL^+] / dt = k_{f(H)}[M'][H_5L'] - k_{r(H)}[MHL^+]. \quad (20)$$

With the overall conditional rate constant ($k_{o(H)}$) determined from a first-order plot, the values of $k_{f(H)}$ and $k_{r(H)}$ are obtained by the following relations:¹²

$$k_{o(H)} = k_{f(H)}[M'] + k_{r(H)} \quad (21)$$

and

$$k_{f(H)} / k_{r(H)} = K / (\alpha_{M(OH)}\alpha_{H_5L(H)}[H^+]^4) \quad (22)$$

The increase in $k_{f(H)}$ with decreasing concentration of hydrogen ion was analyzed from a plot of $k_{f(H)}\alpha_{M(OH)}\alpha_{H_5L(H)}$ against $[H^+]^{-1}$ (Fig. 3) by a least-squares method

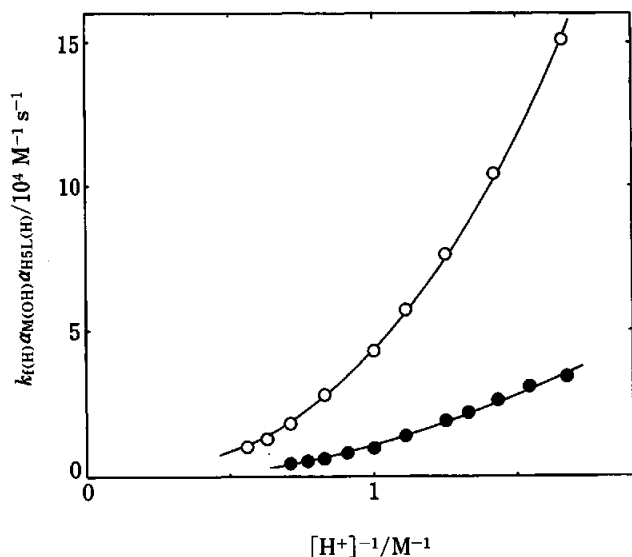


Fig. 3 Plot of $k_{r(H)}\alpha_{M(OH)}\alpha_{H5L(H)}$ against $[H^+]^{-1}$. Conditions: $C_{SXO}=2.51\times 10^{-6}$ M; $C_M/10^{-5}$ M: 2.58 for Zr(IV) (○), 2.61 for Hf(IV) (●); All at 25°C and $I=3$ M. The solid lines are the best-fit curves calculated with the parameters obtained.

to be

$$k_{r(H)}\alpha_{M(OH)}\alpha_{H5L(H)} = k_1[H^+]^{-2} + k_2[H^+]^{-3} \quad (23)$$

for each metal ion. The increase in $k_{r(H)}$ with increasing concentration of hydrogen ion was analyzed as a function of $[H^+]$ to be

$$k_{r(H)} = k_3[H^+] + k_4[H^+]^2 \quad (24)$$

for each metal ion. Then, the rate equation for the reaction (19) can be described as

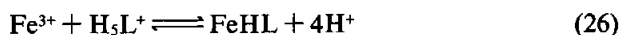
$$\begin{aligned} d[MHL^+]/dt = & k_1[M^{4+}][H_5L^+][H^+]^{-2} \\ & + k_2[M^{4+}][H_5L^+][H^+]^{-3} \\ & - k_3[MHL^+][H^+] \\ & - k_4[MHL^+][H^+]^2. \end{aligned} \quad (25)$$

The rate constants obtained are summarized in Table 1.

Complexation mechanism of Fe(III) with SXO

In order to reasonably explain the proton dependence for the k_1 and k_2 paths in Eq. (25), we studied the complexation reaction of Fe(III) with SXO.

At $[H^+]=0.158, 0.200, 0.251$ and 0.316 M, the absorbance changes at 545 nm, the wavelength of the maximum absorption by the 1 : 1 complex, were analyzed in the same manner as in the case of zirconium and hafnium. The complexation reaction of Fe^{3+} with H_5L^+ was found to be expressed as



with $K=(FeHL)[H^+]^4/(Fe^{3+}[H_5L^+])=10^{1.29}$ and $\epsilon_{FeHL}=5.15\times 10^4$ M⁻¹ cm⁻¹.

Table 1 Rate constants of the complexation reactions of Zr(IV) and Hf(IV) with SXO at 25°C and $I=3$ M (Na,H)ClO₄

	Zr(IV)	Hf(IV)
$\log(k_1/M\ s^{-1})$	4.42	3.84
$\log(k_2/M^2\ s^{-1})$	4.23	3.57
$\log(k_3/M^{-1}\ s^{-1})$	-0.86	-0.60
$\log(k_4/M^{-2}\ s^{-1})$	-0.97	-0.94
$\log(k_{MOH}/M^{-1}\ s^{-1})$	5.28	5.25
$\log(k_{M(OH)_2}/M^{-1}\ s^{-1})$	6.56	6.60
$\log(k_{MOH}^{-H_2O}/s^{-1})$	5.78	5.75
$\log(k_{M(OH)_2}^{-H_2O}/s^{-1})$	7.06	7.10

Under conditions in which $[H^+]=0.150-0.500$ M, $C_{Fe}=5.00\times 10^{-4}$ M, and $C_{SXO}=5.02\times 10^{-6}$ M, the reaction rate was analyzed by the same procedure as in the case of zirconium and hafnium. The rate equation for the formation of FeHL was found to be

$$\begin{aligned} d[FeHL]/dt = & 10^{0.78}[Fe^{3+}][H_5L^+]/[H^+]^2 \\ & - 10^{-0.59}[FeHL][H^+]. \end{aligned} \quad (27)$$

Then, three paths are considered to be possibly relevant to the forward rate (v_f):

$$v_f = (10^{0.78}K_{H5L}K_{H4L})[Fe^{3+}][H_3L^-], \quad (28)$$

$$v_f = (10^{0.78}K_{H5L}/\beta_1)[FeOH^{2+}][H_4L] \quad (29)$$

and

$$v_f = (10^{0.78}/\beta_2)[Fe(OH)_2^+][H_5L^+]. \quad (30)$$

Here, β_i is the overall hydrolysis constant of Fe^{3+} .

With the values of K_{H5L} obtained above and K_{H4L} estimated from the third protonation constant of *N*-methyliminodiacetate ($10^{1.57}$ at 25°C and $I=1.0$)²⁰, we have

$$v_f = 10^{2.59}[Fe^{3+}][H_3L^-] \quad (28')$$

for reaction path (28). Using the values of β_1 and β_2 ,¹⁸ we have the following rate expressions for reaction path (29) and (30), respectively:

$$v_f = 10^{4.07}[FeOH^{2+}][H_4L] \quad (29')$$

and

$$v_f = 10^{7.09}[Fe(OH)_2^+][H_5L^+]. \quad (30')$$

Though we can not stoichiometrically distinguish these three possibilities, we should be able to choose the most probable pathway from all possible alternatives by examining the reasonableness of the respective rate constants (as described below).

Based on the activation volumes for the water-exchange reaction at Fe(III)²¹ and the complexation reaction of Fe(III) with 4-isopropyltropolone²², it has

been established that complexation in aqueous solution involving Fe^{3+} and FeOH^{2+} proceeds *via* an associative interchange (I_a) and dissociative interchange (I_d) mechanisms²³, respectively. Thus, for a complexation reaction involving FeOH^{2+} , the water-exchange rate constant at FeOH^{2+} ($k_{\text{FeOH}}^{-\text{H}_2\text{O}}$) is independent of the coordination characteristics of the complexing agent used, and can be calculated from the second-order rate constant divided by the formation constant of its outersphere complex. For reaction path (29'), the value of $10^{4.57} \text{ s}^{-1}$ is obtained with $10^{-0.50} \text{ M}^{-1}$ (ref. 24) for $K_{\text{os}(\text{FeOH}, \text{H}_4\text{L})}$. This $k_{\text{FeOH}}^{-\text{H}_2\text{O}}$ value is in the range of that reported ($1 \times 10^4 - 4 \times 10^4 \text{ s}^{-1}$).²⁵ For a complexation reaction involving Fe^{3+} , it has been commonly accepted^{22,26} that the rate constant of the reaction of Fe^{3+} is about three orders of magnitude smaller than that of FeOH^{2+} . However, the value of $10^{2.59} \text{ M}^{-1} \text{ s}^{-1}$ calculated for reaction path (28') is significantly larger than the predicted using the above rule. Under an $[\text{H}^+]$ range similar to the present conditions, in no reaction system has a reaction path involving $\text{Fe}(\text{OH})_2^+$ been found. Thus, the respective reactions of Fe^{3+} and $\text{Fe}(\text{OH})_2^+$ with H_3L^- and H_5L^+ cannot be regarded as being important paths: the present complexation should proceed through reaction path (29'), which involves H_4L as the reactive species of SXO.

Complexation mechanism of Zr(IV) and Hf(IV) with SXO

Since the $[\text{H}^+]$ range employed for zirconium and hafnium study is similar to that for Fe(III), it is reasonably assumed that the reacting species of SXO for these tetravalent metal ions is also H_4L . Then, the forward reaction in Eq. (25) can be expressed as

$$\begin{aligned} v_f &= k_1[\text{M}^{4+}][\text{H}_5\text{L}^+][\text{H}^+]^{-2} + k_2[\text{M}^{4+}][\text{H}_5\text{L}^+][\text{H}^+]^{-3} \\ &= (k_1 K_{\text{H}_5\text{L}}/\beta_1)[\text{MOH}^{3+}][\text{H}_4\text{L}] \\ &\quad + (k_2 K_{\text{H}_5\text{L}}/\beta_2)[\text{M}(\text{OH})_2^{2+}][\text{H}_4\text{L}] \\ &= k_{\text{MOH}}[\text{MOH}^{3+}][\text{H}_4\text{L}] + k_{\text{M}(\text{OH})_2}[\text{M}(\text{OH})_2^{2+}][\text{H}_4\text{L}] \end{aligned} \quad (31)$$

and the rate constants k_{MOH} and $k_{\text{M}(\text{OH})_2}$ involved are calculated, as shown in Table 1. These results suggest that a significant difference in reactivity cannot be found between zirconium and hafnium.

The proton dependence for the k_3 and k_4 paths in Eq. (25) may be attributable to the protonation equilibria of MHL^+ : the rapid protonation leading to the formation of MH_2L^{2+} and MH_3L^{3+} is followed by an M-L bond rupture as the rate-determining step.

Bound ligand effect of hydroxide

For a complexation reaction proceeding *via* the I_d mechanism, it has been shown^{7,8} that the water-exchange rate constant at MA ($k_{\text{MA}}^{-\text{H}_2\text{O}}$) is expressed as

$$\begin{aligned} \log(k_{\text{MA}}^{-\text{H}_2\text{O}}/\text{number of H}_2\text{O in MA}) \\ = \log(k_{\text{M}}^{-\text{H}_2\text{O}}/\text{number of H}_2\text{O in M}) + \gamma E(\text{A}). \end{aligned} \quad (32)$$

Assuming that this mechanism is also operative in the

present reaction system and that the hydration number of zirconium and hafnium is 8 for both aqua ions²⁷, the bound ligand effect of the hydroxide ion on the reactivity of these metal ions is described by¹²

$$\log(k_{\text{MA}}^{-\text{H}_2\text{O}}/7) - \log(k_{\text{M}}^{-\text{H}_2\text{O}}/8) = \gamma E(\text{OH}^-) \quad (33)$$

and

$$\log(k_{\text{M}(\text{OH})_2}^{-\text{H}_2\text{O}}/6) - \log(k_{\text{M}}^{-\text{H}_2\text{O}}/8) = 2\gamma E(\text{OH}^-). \quad (34)$$

With $K_{\text{os}(\text{MOH}, \text{H}_4\text{L})} = K_{\text{os}(\text{M}(\text{OH})_2, \text{H}_4\text{L})} = 10^{-0.50} \text{ M}^{-1}$, $k_{\text{MOH}}^{-\text{H}_2\text{O}} = k_{\text{MOH}}/K_{\text{os}(\text{MOH}, \text{H}_4\text{L})}$ and $k_{\text{M}(\text{OH})_2}^{-\text{H}_2\text{O}} = k_{\text{M}(\text{OH})_2}/K_{\text{os}(\text{M}(\text{OH})_2, \text{H}_4\text{L})}$ are calculated as listed in Table 1. With Eqs. (33) and (34), the rate constants in Table 1 and $E(\text{OH}^-) = 1.65$,⁹ the values of γ and $\log k_{\text{M}}^{-\text{H}_2\text{O}}$ for zirconium and hafnium were estimated to be 0.70 and 4.68, and 0.74 and 4.58, respectively.

These γ values are considerably smaller than those predicted by the relationship between γ and σ .²⁸ This difference may be attributable to a change in the mechanism; one possibility is that, as in the case of Fe(III), the complexation of M^{4+} proceeds *via* the I_a mechanism, whereas those of MOH^{3+} and/or $\text{M}(\text{OH})_2^{2+}$ proceed *via* the I_d mechanism. However, as stated previously¹¹, hard metal ions⁹, such as Zr(IV) and Hf(IV), have a larger γ value than do less hard metal ions, such as Co(II) ($\gamma = 0.47$), Ni(II) ($\gamma = 0.40$), and Zn(II) ($\gamma = 0.30$).

Possibilities to design a new kinetic-catalytic method

Using the parameters obtained by the present studies, we now discuss some possibilities to design a new kinetic-catalytic method based on ligand-substitution reactions involving a zirconium or hafnium complex.

For reactions involving zirconium, which has a higher α and β than do hafnium, a higher acceleration effect by a third ligand (A) is anticipated; this effect can be described by

$$\begin{aligned} \log(k_f^\dagger/k_f) &= \alpha E(\text{A}) + \alpha H(\text{A}) + \gamma E(\text{A}) \\ &= 1.45 E(\text{A}) + 1.10 H(\text{A}) + 0.70 E(\text{A}) \\ &= 2.15 E(\text{A}) + 1.10 H(\text{A}). \end{aligned} \quad (35)$$

Using this equation, we find some significant differences in the reactivity between such species as discussed below.

For $\text{A} = \text{SO}_3^{2-}$ and SO_4^{2-} the values of k_f^\dagger are predicted to be $10^{15.5}$ and $10^{5.3}$ times larger than that of k_f , respectively. This marked acceleration effect of SO_3^{2-} and the large difference in reactivity between SO_3^{2-} and SO_4^{2-} provide a possibility to design a new sensitive and selective kinetic method for determining sulfite in the presence of sulfate with this reaction system. The estimation of k_f^\dagger for $\text{A} = \text{NO}_2^-$ and NO_3^- points to the possibility of a similar differential determination of nitrite in the presence of nitrate. The value of k_f^\dagger for $\text{A} = \text{F}^-$ is estimated to be $10^{4.8}$ times larger than that of k_f . Since this acceleration effect is not large enough to design a sensitive method for determining fluoride with this reaction system, the difference in k_f^\dagger ($10^{8.0}$) between $\text{A} = \text{F}^-$

and Cl^- will provide a possibility to design a new selective method for determining fluoride in the presence of chloride.

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References and Notes

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14. For $A=\text{H}_2\text{O}$ in Eq. (2) we have

$$\log(k_{\text{ML}}^{-1}/k_{\text{M}}^{-\text{H}_2\text{O}}) = -\alpha E(\text{L}) - \beta H(\text{L}).$$

It is established that, in most cases, the formation constant of ML is given by

$$K_{\text{ML}} = K_{\text{os}(\text{M,L})} \times (k_{\text{M}}^{-\text{H}_2\text{O}}/k_{\text{ML}}^{-1}).$$

Combining these equations, we have

$$\log K_{\text{ML}} = \log K_{\text{os}(\text{M,L})} + \alpha E(\text{L}) + \beta H(\text{L}).$$

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