Kinetics and mechanism of the ligand exchange reaction in tetrakis(acetylacetonato)hafnium(IV) in C_6D_6

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Abstract

The kinetics of the ligand exchange reaction between tetrakis(acetylacetonato)hafnium(IV), $Hf(acac)_4$ and free acetylacetone (Hacac) in C_6D_6 have been studied by the ^1H NMR line-broadening method. The observed first-order rate constant k_{obs} is expressed as a function of $[Hacac]_{enol}$: $k_{obs} = (k_2 + k_{3,HA})K_{1,HA}[Hacac]_{enol}/(1 + K_{1,HA}[Hacac]_{enol})$, where $[Hacac]_{enol}$ signifies the concentration of Hacac in the enol form and $K_{1,HA}$ is the equilibrium constant for the formation of a nine-coordinate adduct complex $Hf(acac)_4Hacac$. The rate constants k_2 and $k_{3,HA}$ correspond to those of proton transfer from coordinated Hacac to leaving acac and the ring opening of acac in the adduct complex, respectively. The existence of the $k_{3,HA}$ path was evidenced by the deuterium isotope effect on the rate. Activation parameters for the $(k_2 + k_{3,HA})$ path were obtained from the temperature dependence of the $(k_2 + k_{3,HA})$ value: $\Delta H^{\neq} = 41 \pm 2$ kJ mol^{-1} and $\Delta S^{\neq} = -81 \pm 5$ J K^{-1} mol^{-1}. The exchange reaction was accelerated by addition of H_2O to the sample solution. These results are discussed in connection with those of the acac exchange in analogous quadrivalent metal complexes.

Introduction

The large ionic radii (1.14 and 1.19 pm, respectively, for coordination number 8) [1] of uranium(IV) and thorium(IV) complexes enable them to form nine-coordinate adduct complexes. The formation of the adduct complexes has been proposed in studies of kinetics of ligand exchange reactions between $M(acac)_4$ ($M = U^{4+}$ and Th^{4+}) and free acetylacetone (Hacac) [2, 3]. According to the studies, the exchange reactions proceed through nine-coordinate intermediates $M(acac)_4Hacac$, where the unidentate Hacac ligand is of the enol form. The formation of the intermediates is followed by a proton-transfer reaction, the rate of which determines the exchange rate. The mechanism of acac exchange in the $M(acac)_4$ complexes is different from that in the corresponding tervalent metal complexes $M(acac)_3$ [4] in which the central metal ions do not form seven-coordinate adducts because of their small ionic radii.

It is worthwhile to see whether the radius of the M^{4+} ion has an effect on the kinetics and mechanism of the ligand exchange reaction in quadrivalent metal complexes $M(acac)_4$. We chose the $Hf(acac)_4$ complex with a much smaller ionic radius (97 pm for coordination number 8) [1] than the corresponding U(IV) and Th(IV) complexes. Very little information is available for ligand substitution of Hf(IV) complexes. Adams and Larsen [5] reported the kinetics and mechanism of the ligand exchange reaction between $Hf(acac)_4$ and free Hacac in C_6H_5Cl and C_6H_6, but the mechanism remains ambiguous. In this paper we report the kinetic results of the exchange reaction of the $Hf(acac)_4$ complex with free Hacac in C_6D_6 and compare them with earlier results.

Experimental

Materials

Hafnium oxychloride 8-hydrate ($HfOCl_2 \cdot 8H_2O$) was prepared by dissolving $HfCl_4$ (Aldrich) in dilute HCl solution. The synthetic method for obtaining the $Hf(acac)_4$ complex from hafnium oxychloride 8-hydrate was similar to that for $Zr(acac)_4$ from zirconium oxychloride 8-hydrate($ZrOCl_2 \cdot 8H_2O$) [6]. The complex was recrystallized from a mixture of benzene and petroleum

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ether and dried under vacuum. Acetylacetone-d_2 was prepared by mixing acetylacetone with D_2O in a volume ratio of 4:1 at 80 °C. This deuteration was repeated four times. The fraction (α) of deuterium incorporation was c. 90%, as determined by comparison of integrated ^1H NMR signals. Benzene-d_6 (Merck) was dried over 4 Å molecular sieves and distilled before use. The water content of NMR sample solutions was analyzed by a Mitsubishi moisture meter (model CA-02).

Measurements of NMR spectra

The measurements of ^1H NMR spectra were carried out on a JEOL JNM-FX 100 FT-NMR spectrometer equipped with a JEOL NM-PVTS1 temperature controller, which was calibrated directly by use of a digital resistance thermometer (Tsuruga Electric Work, Ltd.).

Determination of the enol–keto equilibrium constants for acetylacetone

The concentrations of enol and keto isomers of acetylacetone ([Hacac]$_{enol}$ and [Hacac]$_{keto}$) in C_6D_6 were calculated from the ratio of areas of the methyl proton signals of the enol and keto isomers. Enthalpy and entropy values of the isomerization reaction were determined from the temperature dependence of the equilibrium constant K, which is equal to [Hacac]$_{enol}$/[Hacac]$_{keto}$: $\Delta H = -6.9$ kJ mol^{-1} and $\Delta S = -4.8$ J K^{-1} mol^{-1}.

Kinetic analysis

The ranges of [Hf(acac)$_4$] and [Hacac]$_{total}$ used in the kinetic study were between 0.05 and 0.07 and 0.1 and 0.4 mol kg^{-1}, respectively. The observed first-order rate constants of the ligand exchange reactions were determined from the line-shape analysis of methine proton signals of free Hacac and coordinated acac in Hf(acac)$_4$ by using the two-site model [2, 3].

Results

Figure 1 shows the ^1H NMR spectrum of a mixture of Hf(acac)$_4$ and Hacac in C_6D_6. Each signal is assigned as follows: a and e, methyl and methine protons of the enol isomer of free Hacac; b and d, methyl and methylene protons of the keto isomer of free Hacac; c and f, methyl and methine protons of coordinated acac in Hf(acac)$_4$; g, proton of C_6D_5H.

As the temperature was raised, the a, c, e and f signals were broadened, but the b and d signals were unchanged. This indicates that only the enol isomer exchanges with the coordinated acac. As shown in Fig. 2, the e and f signals were broadened with increasing temperature. This line broadening is attributed to the
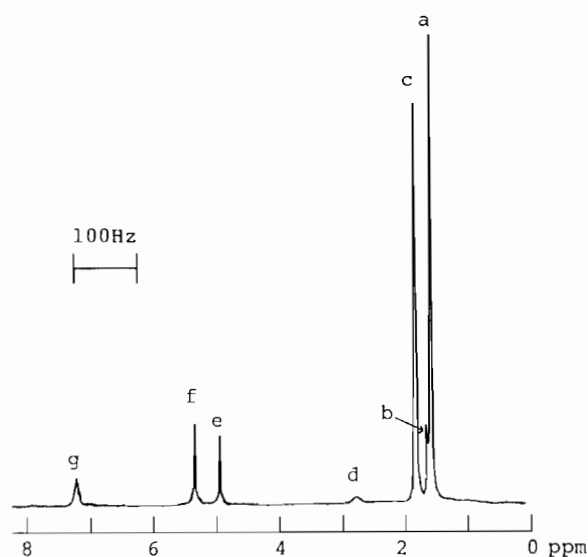

Fig. 1. ^1H NMR spectrum of the mixture of Hf(acac)$_4$ and Hacac in C_6D_6 at 10 °C· [Hf(acac)$_4$] = 0 0500 mol kg^{-1} and [Hacac] = 0.215 mol kg^{-1}.

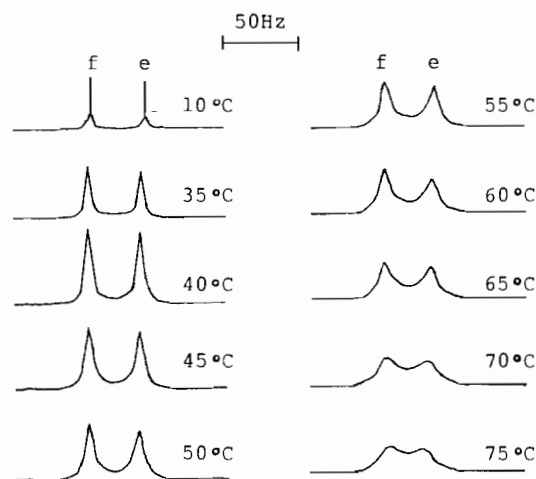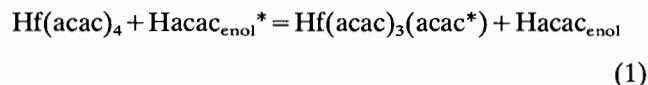
Fig. 2. Temperature dependence of the methine proton signals (e and f signals in Fig 1) of the mixture of Hf(acac)$_4$ and Hacac in C_6D_6: [Hf(acac)$_4$] = 0.0500 mol kg^{-1} and [Hacac] = 0.215 mol kg^{-1}.

ligand exchange reaction between Hf(acac)$_4$ and Hacac in the enol form (Hacac$_{enol}$):

$$Hf(acac)_4 + Hacac_{enol}{}^* = Hf(acac)_3(acac^*) + Hacac_{enol}$$

(1)

where the asterisk is for typographical distinction only. The observed first-order rate constant k_{obs} for reaction (1) is expressed as in eqn. (2).

$$k_{obs} = 4\tau_c{}^{-1} = rate/[Hf(acac)_4]$$

(2)

where τ_c is the lifetime of acac in the Hf(acac)$_4$ complex and can be calculated by using the two-site model for the e and f signals.

The dependence of the k_{obs} values on $[Hacac]_{enol}$ is shown in Fig. 3, where k_{obs} increases with increasing $[Hacac]_{enol}$ in its low region but tends to level off in its high region. Plots of $1/k_{obs}$ against $1/[Hacac]_{enol}$ give straight lines with intercepts as shown in Fig. 4 and yield the expression

$$1/k_{obs} = q + r/[Hacac]_{enol} \qquad (3)$$

The values of q and r obtained from Fig. 4 are given in Table 1.

In order to examine the effect of H_2O on the rate, H_2O ($<3 \times 10^{-3}$ mol kg^{-1}) was added to the sample solutions. The k_{obs} values increased linearly with $[H_2O]$ and the slope was found to be 1.6×10^3 mol^{-1} kg s^{-1} at 35 °C.

The deuterium isotope effect on the rate was also studied using acetylacetone-d$_2$ (Dacac). Figure 5 shows that the k_{obs} values decrease linearly with increasing the fraction (α) of deuteration of Hacac$_{enol}$. The values of α studied were not high, because the kinetic analysis was made on the basis of the ^1H NMR signals of the methine proton of Hacac$_{enol}$. The values of $k_{obs}{}^D$, which

TABLE 1. Kinetic parameters for the acac exchange reaction of Hf(acac)$_4$ in C_6D_6

Temperature (°C)	q^{-1} or $(k_2 + k_{3, HA})$[a] (s^{-1})	q/r or $K_{1, HA}$ (mol^{-1} kg)
35	38 ± 6	24 ± 7
40	52 ± 2	25 ± 2
45	75 ± 9	18 ± 2
50	98 ± 13	18 ± 1
55	123 ± 29	18 ± 4
60	154 ± 44	17 ± 1
65	177 ± 20	20 ± 2
70	230 ± 34	16 ± 5
75	280 ± 46	15 ± 6

[a]$\Delta H^* = 41 \pm 2$ kJ mol^{-1} and $\Delta S^* = -81 \pm 5$ J K^{-1} mol^{-1}.

Fig. 5. Plots of k_{obs} vs. the fraction of Dacac in the enol form in C_6D_6 at various temperatures: $[Hf(acac)_4] = 0.0500$ mol kg^{-1} and $[Hacac] + [Dacac] = 0.200$ mol kg^{-1}.
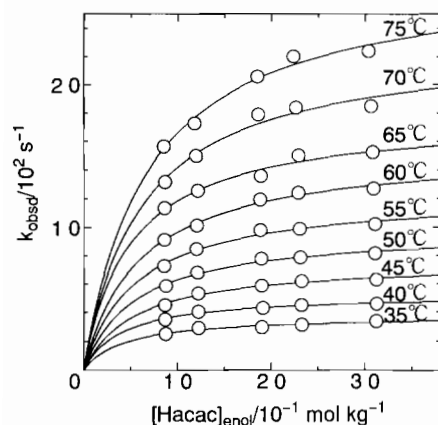

Fig. 3. Plots of k_{obs} vs. $[Hacac]_{enol}$ for the acac exchange of Hf(acac)$_4$ in C_6D_6 at various temperatures.
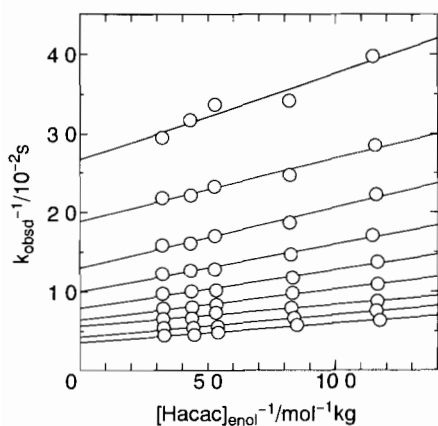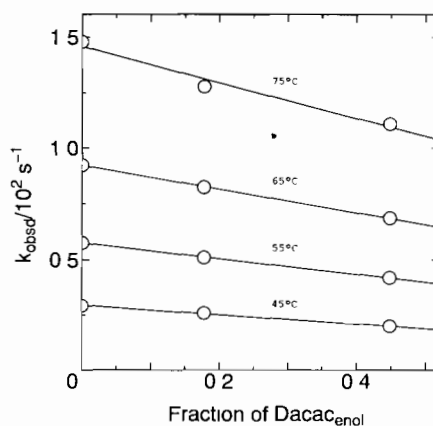

Fig. 4. Plots of $k_{obs}{}^{-1}$ vs. $[Hacac]_{enol}{}^{-1}$ for the acac exchange of Hf(acac)$_4$ in C_6D_6 at various temperatures.

are the observed first-order rate constants for $\alpha = 1$, were estimated from extrapolation of the plots to 100% deuteration. The kinetic isotope effects (KIE) $k_{obs}{}^H/k_{obs}{}^D$ were determined to be 3.3, 2.4, 2.3 and 2.2 at 45, 55, 65 and 75 °C, respectively.

Discussion

The rate law in this study is similar to that for the exchange reaction of acac in the U(acac)$_4$ complex in C_6D_6. This might be well explained by the mechanism given in Fig. 6. According to the mechanism, there is a fast pre-equilibrium reaction between Hf(acac)$_4$ and Hacac$_{enol}$. The reaction leads to the formation of a nine-coordinate adduct complex Hf(acac)$_4$Hacac as an intermediate, where Hacac is coordinated as a unidentate ligand. Two parallel rate-determining processes (k_2 and $k_{3, HA}$ paths) follow the pre-equilibrium reaction. The rate constants k_2 and $k_{3, HA}$ correspond to those of proton transfer from coordinated Hacac to leaving acac and the ring opening of acac in the adduct complex,
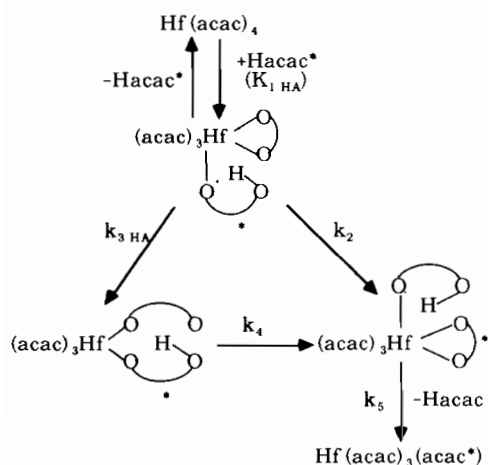
Hf(acac)$_4$

$-$Hacac* | $+$Hacac* ($K_{1\,HA}$)

(acac)$_3$Hf

$k_{3\,HA}$ | k_2

(acac)$_3$Hf | k_4 | (acac)$_3$Hf

k_5 | $-$Hacac

Hf(acac)$_3$(acac*)

Fig. 6. Possible mechanism for the acac exchange between Hf(acac)$_4$ and Hacac ⌒OH and ⌒O represent Hacac in the enol form and acac, respectively.

respectively. If the rate-determining steps are the k_2 and $k_{3,\,HA}$ paths, then k_{obs} is expressed as

$$k_{obs} = \frac{(k_2 + k_{3,\,HA})K_{1,\,HA}[\text{Hacac}]_{enol}}{1 + K_{1,\,HA}[\text{Hacac}]_{enol}} \quad (4a)$$

or

$$1/k_{obs} = 1/(k_2 + k_{3,\,HA})$$
$$+ 1/\{(k_2 + k_{3,\,HA})K_{1,\,HA}[\text{Hacac}]_{enol}\} \quad (4b)$$

Equation (4b) is of the same form as eqn. (3), where constants q and r correspond to $1/(k_2 + k_{3,\,HA})$ and $1/(k_2 + k_{3,\,HA})K_{1,\,HA}$, respectively. The values $(k_2 + k_{3,\,HA})$ and $K_{1,\,HA}$ calculated from the values q and r are given in Table 1.

The addition of H_2O may have an effect on the rate of the acac exchange reactions in $M(acac)_4$ in two different ways. One effect of the addition of H_2O on the rate is the acceleration of the rate, because H_2O acts as a proton acceptor and donor through hydrogen bonding [7] with the nine-coordinate complex. The other effect is the retardation of the rate. This effect is explained by the fact that added H_2O can retard the coordination of Hacac$_{enol}$ to the ninth coordination site of $M(acac)_4$, as in the case of the acac exchange in $Th(acac)_4$ [3]. The linear dependence of the exchange rate on $[H_2O]$ indicates that the former effect may be the predominant effect of added H_2O on the rate in this reaction system. The structure of a transition state involving H_2O is assumed as written below

$$\left(\text{(acac)}_3\text{Hf} \right)^{\ddagger}$$
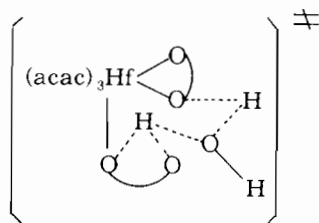
In order to confirm the mechanism suggested in Fig. 6, the deuterium isotope effect on the exchange rate was examined. These KIEs in this study are much smaller than that (c. 9) for the acac exchange in $Th(acac)_4$ in CD_3CN [8], where the proton-transfer process preceded by the formation of $Th(acac)_4$Hacac determines the exchange reaction rate. The latter KIE is close to the maximum KIE, which is estimated from the difference in the zero-point energies of O–H and O–D bonds in Hacac (HA) and Dacac (DA) in their ground states, respectively [9]. If the transition states in the proton transfer have not the same energy for both isotopes, the observed KIE will be smaller than the maximum KIE [10]. According to eqn. (4a), the KIE is equal to the ratio of $(k_2^H + k_{3,\,HA})/(k_2^D + k_{3,\,DA})$. Since the $k_{3,\,DA}$ value is assumed to be the same as the $k_{3,\,HA}$ value, the magnitude of KIE depends on relative magnitude of $k_2^H(=k_2)$ and $k_{3,\,HA}$ values. If k_2^H is much larger than $k_{3,\,HA}$, the KIE approaches to k_2^H/k_2^D, which is the case for $Th(acac)_4$. But if $k_{3,\,HA}$ is not negligible compared with k_2^H, then the KIE will be smaller than k_2^H/k_2^D. The contribution of $k_{3,\,HA}$ to k_{obs} is expected to be larger as the ionic radius of a metal ion is smaller. The deuterium isotope effect in this study leads to exclude the possibility of the mechanism suggested by Adams and Larsen [5], where the rate-determining step is the k_5 path.

In conclusion the ionic radius of a central metal ion has no effect of the mechanism of acac exchange in $M(acac)_4$ complexes. The rate-determining steps are two parallel paths, where one is the proton transfer from Hacac to acac in a nine-coordinate complex $M(acac)_4$Hacac and the other is the ring opening of acac in the complex. The difference in rates for the acac exchange can be explained by the difference in ionic radii of the central metal ions: for the $M(acac)_4$ complex of a large metal ion a unidentate Hacac ligand in the nine-coordinate intermediate $M(acac)_4$Hacac can easily orient so as to favor proton transfer, resulting in a fast exchange reaction rate.

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