Kinetics and Mechanism of Ligand Exchange in Tetrakis(acetylacetonato)zirconium(IV) in Organic Solvents

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The kinetics of ligand exchange between [Zr(acac)$_4$] (acac = acetylacetonate) and free acetylacetone (Hacac) in various organic solvents such as $CDCl_3$, C_6D_6 and CD_3CN has been studied by the ^1H NMR line-broadening method. The observed first-order rate constant k_{obs} for acac exchange in $CDCl_3$ and C_6D_6 is expressed as a function of concentration of Hacac in the enol form: $k_{obs} = (k_2 + k_{3,HA})K_1[\mathrm{Hacac}]_{enol}/(1 + K_1[\mathrm{Hacac}]_{enol})$, where K_1 is the equilibrium constant for the formation of the nine-co-ordinate adduct [Zr(acac)$_4$(Hacac)]. The rate constants k_2 and $k_{3,HA}$ correspond to those of proton transfer from co-ordinated Hacac to leaving acac and ring opening of acac in the adduct, respectively. Activation parameters $\Delta H^‡$/kJ mol^{-1} and $\Delta S^‡$/J K^{-1} mol^{-1} for the $k_2 + k_{3,HA}$ path are 33.7 ± 2.3, −87.8 ± 8.1 in $CDCl_3$ and 38.1 ± 0.1, −85.9 ± 0.4 in C_6D_6. The rate constants k_{obs} in CD_3CN are much smaller than those in $CDCl_3$ and C_6D_6, and increase linearly with increasing [Hacac]$_{enol}$. Addition of water and dimethyl sulfoxide to C_6D_6 solutions results in acceleration and retardation of the exchange rate, respectively. The deuterium kinetic isotope effect was observed by using [$^2H_2$]acetylacetone in place of Hacac in C_6D_6. The results are discussed in connection with those of acac exchange in other [M(acac)$_4$] complexes (M = Hf^{4+}, Ce^{4+}, Th^{4+} or U^{4+}).

Zirconium alloy is widely used as a fuel cladding material in nuclear reactors, since the thermal neutron absorption cross section of zirconium is relatively low compared with other metals. In nuclear fuel processes, spent fuels, which contain zirconium together with a variety of actinoids and fission products, are dissolved in highly acidic solutions in order to recover the uranium and plutonium. β-Diketonato chelates are used as solvent-extraction reagents for actinoids in the reprocessing of spent fuel and the separation of elements from fission products.[1] It is, therefore, of particular importance that we understand the chemical properties of the tetrakis(β-diketonato) complexes of zirconium(IV) in solution. However little information is available on the solution chemistry of such compounds.[2–6]

In this paper we report the results of a kinetic study of ligand exchange in tetrakis(acetylacetonato)zirconium(IV), [Zr(acac)$_4$]. Little information is known about ligand-exchange and substitution reactions in zirconium(IV) complexes.[4] Adams and Larsen[4] reported the kinetics and mechanism of the ligand-exchange reaction between [Zr(acac)$_4$] and free Hacac in C_6H_5Cl and C_6H_6. According to the mechanism, the reaction is initiated by ring opening of one co-ordinated acac. On the other hand, it was suggested that ligand exchange in [M(acac)$_4$] (M = Hf^{4+}, Ce^{4+}, Th^{4+} or U^{4+} is initiated by the formation of a nine-co-ordinate adduct, [M(acac)$_4$(Hacac)], followed by two parallel rate-determining steps.[7–11] The two steps are proton transfer from co-ordinated Hacac to leaving acac and ring opening of acac in the adduct. The mechanism of acac exchange in [M(acac)$_4$] is considerably different from that in [M(acac)$_3$] (M = a variety of tervalent metal ions),[12] the rate-determining step of acac exchange in the latter being ring-opening of a chelate ring with the aid of incoming Hacac.

It was also of interest to us to investigate the effect of ionic radius on the kinetics and mechanism of ligand exchange in [M(acac)$_4$]. The effective ionic radius of the Zr^{4+} ion (84 pm for co-ordination number eight) is nearly the same as that (83 pm) of Hf^{4+}.[13] The complex [Zr(acac)$_4$] has the same eight-co-ordinate square-antiprismatic structure as other [M(acac)$_4$] complexes.[14]

Experimental

Materials.—The complex [Zr(acac)$_4$] (Kanto Chemical) was recrystallized from benzene–acetylacetone (10:1, v/v) and the white crystals obtained washed with cold benzene and dried *in vacuo*. Acetylacetone (Kanto) was dried over anhydrous magnesium sulfate and distilled twice. Dimethyl sulfoxide (dmso) (Kanto) was dried over 3 Å molecular sieves (Wako Pure Chemical) and distilled under reduced pressure. [$^2H_6$]-Benzene, [$^2H_1$]chloroform and [$^2H_3$]acetonitrile (Merck) were dried over 4 Å molecular sieves and distilled before use. [$^2H_2$]Acetylacetone was prepared as described in a previous paper.[10] The water content in NMR sample solutions was determined by a Mitsubishi moisture meter (model CA-02).

Measurements of NMR Spectra.—The ^1H NMR spectra were recorded 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).

Kinetic Analysis.—The observed first-order rate constants of acac exchange in [Zr(acac)$_4$] were determined from line-shape analysis of the methine proton signals of free Hacac and co-ordinated acac by using the two-site model.[7,8]

Results

NMR Spectra.—The ^1H NMR spectra of a mixture of [Zr(acac)$_4$] and Hacac in C_6D_6 were measured at various temperatures (Fig. 1). The signals at 35 °C are assigned as follows: a, C_6D_5H proton; b and e, methine and methyl protons of co-ordinated acac in [Zr(acac)$_4$]; c and g, methine and methyl protons of the enol isomer of free Hacac; d and f, methylene and methyl protons of the keto isomer of free Hacac. As the

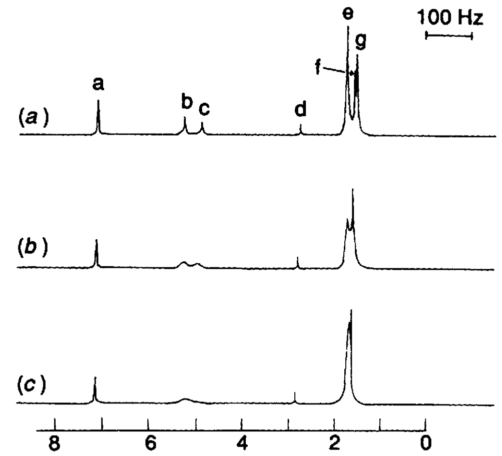

Fig. 1 Proton NMR spectra of a mixture $[Zr(acac)_4]$ and Hacac in C_6D_6 at (a) 35, (b) 55 and (c) 75 °C: $[Zr(acac)_4]$ = 0.0500 mol kg^{-1} and $[Hacac]_{total}$ = 0.190 mol kg^{-1}

temperature increased signals b and c tended to coalesce, which is attributed to ligand exchange between $[Zr(acac)_4]$ and free $Hacac_{enol}$. The keto isomer of free Hacac does not interact with $[Zr(acac)_4]$.

The ligand-exchange reaction between $[Zr(acac)_4]$ and $Hacac_{enol}$ can be expressed by equation (1) and the observed

$$[Zr(acac)_4] + Hacac_{enol}{}^* \rightleftharpoons [Zr(acac)_3(acac^*)] + Hacac_{enol} \quad (1)$$

first-order constant k_{obs} by equation (2), where τ_c is the lifetime

$$k_{obs} = 4\tau_c^{-1} = \text{rate}/[Zr(acac)_4] \quad (2)$$

of acac in $[Zr(acac)_4]$ and can be calculated using the two-site model for signals b and c.

Equilibrium between Keto and Enol Isomers of Hacac.—The concentrations of the enol and keto isomers of free Hacac were obtained from the ratio of the areas of the methyl proton signals of the isomers under the same kinetic conditions. From the temperature dependence of the equilibrium constant, $K_a(=[Hacac]_{enol}/[Hacac]_{keto})$, the thermodynamic parameters $\Delta H°$/kJ mol^{-1} and $\Delta S°$/J K^{-1} mol^{-1} were calculated as follows: −6.9 ± 0.1 and −4.8 ± 1.1; −8.0 ± 0.2 and −12.4 ± 0.8; −6.4 ± 0.1 and −18.0 ± 0.4 in C_6D_6, $CDCl_3$ and CD_3CN, respectively.[15,*]

Exchange Reactions between $[Zr(acac)_4]$ *and* $Hacac_{enol}$.—The k_{obs} values were independent of $[Zr(acac)_4]$ but dependent on $[Hacac]_{enol}$ in C_6D_6. Plots of k_{obs} *vs.* $[Hacac]_{enol}$ at various temperatures showed that the k_{obs} depended linearly on $[Hacac]_{enol}$ in its low region and tended to approach limiting values in its high region, as observed in corresponding exchange reactions in other $[M(acac)_4]$ ($M = Hf^{4+}$, Ce^{4+} or U^{4+}) complexes. Plots of $1/k_{obs}$ against $1/[Hacac]_{enol}$ give straight lines with intercepts as shown in Fig. 2 and yield expression (3).

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

The dependence of k_{obs} on $[Hacac]_{enol}$ in $CDCl_3$ had the same trend as that observed in C_6D_6. In the case of CD_3CN, the k_{obs} values increase linearly with increasing $[Hacac]_{enol}$ with intercepts, as illustrated in Fig. 3, the plots of which are expressed by $k_{obs} = s + t\,[Hacac]_{enol}$.

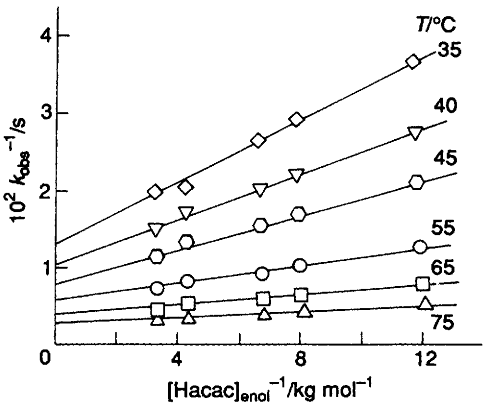

Fig. 2 Plots of $1/k_{obs}$ *vs.* $1/[Hacac]_{enol}$ for acac exchange in $[Zr(acac)_4]$ in C_6D_6 at various temperatures

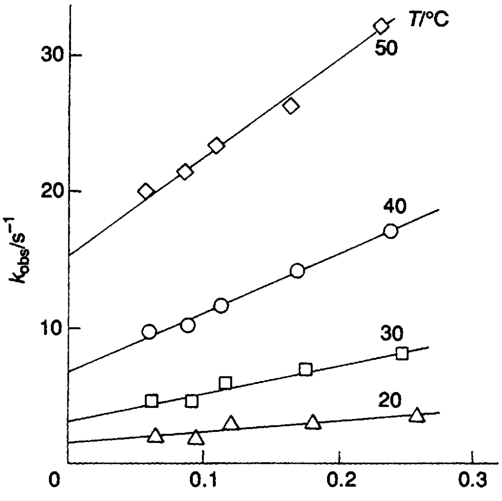

Fig. 3 Plots of k_{obs} *vs.* $[Hacac]_{enol}$ for acac exchange in $[Zr(acac)_4]$ in CD_3CN at various temperatures

Effect of Added H_2O *and dmso on the Exchange Rate.*—Water was added ($[H_2O] < 4 \times 10^{-2}$ mol kg^{-1}) to the C_6D_6 solutions in order to examine its effect on the exchange rate. The k_{obs} values increased linearly with $[H_2O]$, as in the corresponding exchange reactions in $[Hf(acac)_4]$.[10]

Addition of dmso ([dmso] < 0.67 mol kg^{-1}) to the C_6D_6 solutions resulted in a remarkable retardation of the exchange rate, as shown in Fig. 4. The rate constants decreased smoothly with increasing [dmso] and consequently approached constant values at higher [dmso]. As shown in Fig. 5, plots of $1/k_{obs}$ against [dmso] gave straight lines in the [dmso] range studied: $1/k_{obs} = u + v[\text{dmso}]$.

Deuterium Isotope Effect on the Exchange Rate.—The effect of deuterium on the exchange rate was studied using $[^2H_2]$acetylacetone (Dacac). There was a linear relationship between k_{obs} and the fraction (α) of deuteriation of $Hacac_{enol}$. Values of $k_{obs}{}^D$, which are the observed first-order rate constants for α = 1, were estimated by extrapolating the linear k_{obs} *vs.* α plots to α = 1. The kinetic isotope effect, $k_{obs}{}^H/k_{obs}{}^D$, was determined to be 2.3, 2.0, 1.7 and 1.5 at 40, 50, 60 and 65 °C, respectively.

Discussion

The dependence of k_{obs} on $[Hacac]_{enol}$, the effect of added H_2O on the rate and the kinetic isotope effects are summarized in Table 1 for acac exchange in [M(acac)] complexes. The dependence of k_{obs} on $[Hacac]_{enol}$ in each organic solvent is very similar among the $[M(acac)_4]$ complexes, and the effect of

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[*] The enthalpy in pure acetylacetone was calculated to be −11.3 ± 0.4 kJ mol^{-1}.

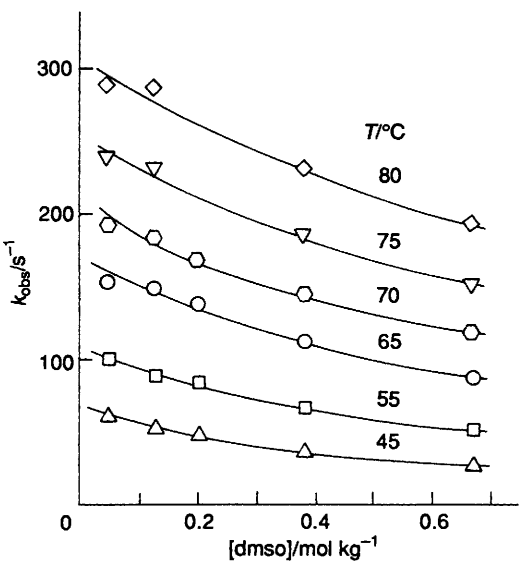

Fig. 4 Plots of k_{obs} *vs.* [dmso] for acac exchange in $[Zr(acac)_4]$ in C_6D_6 at various temperatures: $[Zr(acac)_4] = 0.0500$ mol kg^{-1} and $[Hacac]_{total} = 0.268$ mol kg^{-1}

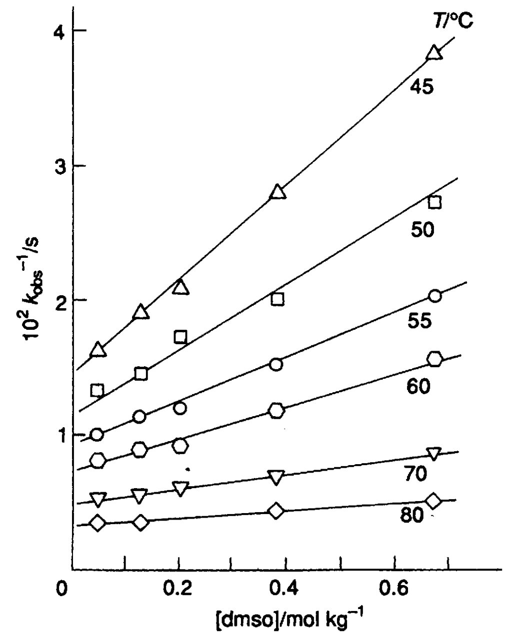

Fig. 5 Plots of $1/k_{obs}$ *vs.* [dmso] for acac exchange in $[Zr(acac)_4]$ in C_6D_6 at various temperatures: $[Zr(acac)_4] = 0.0500$ mol kg^{-1} and $[Hacac]_{total} = 0.268$ mol kg^{-1}

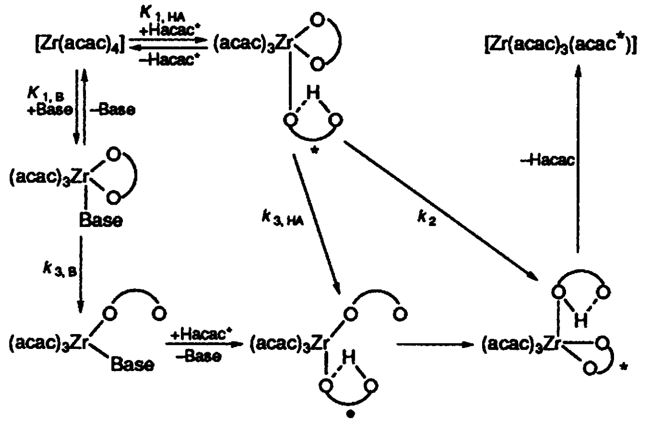

Fig. 6 Possible mechanism for acac exchange between $[Zr(acac)_4]$ and free Hacac: O⌒OH and O⌒O represent Hcac in the enol form and acac, respectively

added H_2O on the rate in $[Zr(acac)_4]$ is the same as that in $[Hf(acac)_4]$ but different from those in $[Ce(acac)_4]$ or $[Th(acac)_4]$. The retardation effect of added dmso is observed for all the $[M(acac)_4]$ (M = Zr^{4+}, Ce^{4+}, U^{4+} or Th^{4+}) complexes studied.

The ligand-exchange reaction in $[Zr(acac)_4]$ might be well explained by the mechanism shown in Fig. 6, which is likely to be the case for the other $[M(acac)_4]$ complexes. The exchange reaction is initiated by fast pre-equilibrium reactions between $[Zr(acac)_4]$ and $Hacac_{enol}$ (HA) or a base (B; in the text base refers to a unidentate ligand such as H_2O, dmso or CD_3CN), the equilibrium constants of which are $K_{1,HA}$ and $K_{1,B}$, respectively. The reactions lead to the formation of nine-co-ordinate adducts $[Zr(acac)_4(Hacac)]$ or $[Zr(acac)_4B]$ as intermediates, the ninth co-ordination site being occupied by a unidentate ligand. The fast pre-equilibrium reactions are followed by three parallel rate-determining processes (k_2, $k_{3,HA}$ and $k_{3,B}$). The rate constants k_2 and $k_{3,HA}$ (or $k_{3,B}$) correspond to proton transfer from co-ordinated Hacac to leaving acac and ring opening of one acac chelate ring in the adduct respectively. According to the mechanism, the k_{obs} is expressed by equation (4).

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

The dependence of k_{obs} on $[Hacac]_{enol}$ in C_6D_6 or $CDCl_3$, which have no co-ordinating ability, can be explained by equations (5a) or (5b) which are obtained by putting [B] equal to zero in equation (4).

$$k_{obs} = \frac{(k_2 + k_{3,HA})K_{1,HA}[Hacac]_{enol}}{1 + K_{1,HA}[Hacac]_{enol}} \qquad (5a)$$

$$1/k_{obs} = 1/(k_2 + k_{3,HA}) + 1/\{(k_2 + k_{3,HA})K_{1,HA}[Hacac]_{enol}\} \qquad (5b)$$

Equation (5b) is of the same form as equation (3) and explains the linear plots in Fig. 2, where the slopes and intercepts correspond to $1/(k_2 + k_{3,HA})K_{1,HA}$ and $1/(k_2 + k_{3,HA})$, respectively. The activation parameters for ($k_2 + k_{3,HA}$) are listed in Table 2, together with those for other $[M(acac)_4]$ complexes. The thermodynamic parameters $\Delta H°$/kJ mol^{-1} and $\Delta S°$/J K^{-1} mol^{-1} for $K_{1,HA}$ are as follows: 4.1 ± 0.5 and 31 ± 8 in C_6D_6; 2.5 ± 0.2 and 13 ± 3 in $CDCl_3$. The $k_2 + k_{3,HA}$ values are much larger in $CDCl_3$ than in C_6D_6, as for acac exchange in $[U(acac)_4]$.[8] It is noted that the rate of substitution of dibenzoylmethanate for acac in $[UO_2(acac)_2L]$ (L = unidentate ligand) is also too fast in view of the low relative permittivity of chloroform.[16] The rate constant of the reaction between a negatively charged ion and a dipole such as the proton-transfer reaction in this study increases as the relative permittivity of the medium increases.[17] The reason why the rate in chloroform is abnormally fast is not fully understood.

The exchange rate in this study is much slower in CD_3CN than in C_6D_6, in spite of the fact that the relative permittivity (39.95 at 25 °C) of acetonitrile is much higher than that (2.28 at 25 °C) of benzene. This result is attributed to the fact that CD_3CN acts as a base. If the solvent is CD_3CN (denoted solv: [solv] = 23 mol kg^{-1}) and $1 + K_{1,solv}[solv] \gg K_{1,HA}[Hacac]_{enol}$, then equation (4) can be rewritten into the form of equation (6).

Table 1 Dependence of k_{obs} on $[Hacac]_{enol}$, the effect of added H_2O and kinetic isotopic effect for the acac exchange in $[M(acac)_4]$ in organic solvents

M	Radius*/pm	k_{obs} *vs.* $[Hacac]_{enol}$, solvent	k_{obs} *vs.* $[H_2O]$	Kinetic isotope effect (T/°C)	Ref.
Hf^{4+}	83	$1/k_{obs} = q + r/[Hacac]_{enol}$, C_6D_6	$k_{obs} = u + v[H_2O]$	3.3 (45)	10
Zr^{4+}	84	$1/k_{obs} = q + r/[Hacac]_{enol}$, C_6D_6	$k_{obs} = u + v[H_2O]$	2.3 (40)	This work
		$1/k_{obs} = q + r/[Hacac]_{enol}$, $CDCl_3$			
		$k_{obs} = s + t[Hacac]_{enol}$, CD_3CN			
Ce^{4+}	97	$1/k_{obs} = q + r/[Hacac]_{enol}$, C_6D_6	k_{obs} = constant	4.2 (40)	11
		$k_{obs} = s + t[Hacac]_{enol}$, CD_3CN			
U^{4+}	100	$1/k_{obs} = q + r/[Hacac]_{enol}$, C_6D_6			8
		$k_{obs} = t[Hacac]_{enol}$, $CDCl_3$			
		$k_{obs} = s + t[Hacac]_{enol}$, CD_3CN			
Th^{4+}	105	$k_{obs} = t[Hacac]_{enol}$, $CDCl_3$			7
		$k_{obs} = t[Hacac]_{enol}$, CD_3CN	$1/k_{obs} = u + v[H_2O]$	8.9 (20)	9

* The effective ionic radius for co-ordination number eight.

Table 2 Activation parameters for $(k_2 + k_{3,HA})$ or $(k_2 + k_{3,HA})K_{1,HA}$ for acac exchange in $[M(acac)_4]$ in organic solvents

Complex	Solvent	Rate constant[a,b] at 25 °C	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	Ref.
$[Hf(acac)_4]$	C_6D_6	23.7[a]	41 ± 2	−81 ± 5	10
$[Zr(acac)_4]$	C_6D_6	46.1[a]	38.1 ± 0.1	−85.9 ± 0.4	This work
	$CDCl_3$	215[a]	33.7 ± 2.3	−87.8 ± 8.1	This work
$[Ce(acac)_4]$	C_6D_6	15.7[a]	30.7 ± 0.1	−119 ± 51	11
$[U(acac)_4]$	C_6D_6	293[a]	40.4 ± 0.6	−62.6 ± 2.1	8
	$CDCl_3$	1.2×10^3[b]	37.6 ± 0.9	−59.8 ± 3.0	8
$[Th(acac)_4]$	$CDCl_3$	1.4×10^3[b]	30.8 ± 0.7	−81.3 ± 2.5	7
	CD_3CN	375[b]	30.2 ± 1.0	−97.3 ± 3.5	7

[a] $(k_2 + k_{3,HA})/s^{-1}$. [b] $(k_2 + k_{3,HA})K_{1,HA}/kg\ mol^{-1}\ s^{-1}$.

$$k_{obs} = \frac{k_{3,solv}K_{1,solv}[solv]}{1 + K_{1,solv}[solv]} + \frac{(k_2 + k_{3,HA})K_{1,HA}}{1 + K_{1,solv}[solv]}[Hacac]_{enol} \quad (6)$$

The linear plots in Fig. 3 are explained by equation (6). The existence of intercepts indicates that the ring-opening process in the adduct $[Zr(acac)_4(CD_3CN)]$ makes some contribution to the exchange reaction in $[Zr(acac)_4]$, as in $[U(acac)_4]$[8] and $[Ce(acac)_4]$.[11] The fact that plots of k_{obs} against $[Hacac]_{enol}$ are linear without intercepts for acac exchange in $[Th(acac)_4]$ in CD_3CN[7] indicates that the ring-opening process is negligibly slow compared to the k_2 process in the acac exchange. Assuming that $K_{1,solv}[solv] \gg 1$ in equation (6), then the intercepts in Fig. 3 become equal to $k_{3,solv}$ values of 1.5, 3.1, 6.8 and 15.4 s^{-1} at 20, 30, 40 and 50 °C, respectively.

The effect of added dmso on the rate (Fig. 4) can be explained well by equation (4), which shows that when the ratio of $(k_2 + k_{3,HA})K_{1,HA}[Hacac]_{enol}/(1 + K_{1,HA}[Hacac]_{enol})$ is larger than $k_{3,dmso}$, the k_{obs} values decrease with increasing [dmso] and approach constant values ($k_{3,dmso}$) at very high [dmso]. The fact that the $k_{3,dmso}$ values are not zero in Fig. 4 also supports the existence of the ring-opening process in the nine-co-ordinate adduct $[Zr(acac)_4(dmso)]$. On the assumption that $(k_2 + k_{3,HA})K_{1,HA}[Hacac]_{enol} \gg k_{3,dmso}K_{1,dmso}[dmso]$, equation (4) can be expressed by equation (7a) and (7b). The linear plots of $1/k_{obs}$ *vs.* [dmso] in Fig. 5 are explained well by equation (7b).

$$k_{obs} = \frac{(k_2 + k_{3,HA})K_{1,HA}[Hacac]_{enol}}{1 + K_{1,HA}[Hacac]_{enol} + K_{1,dmso}[dmso]} \quad (7a)$$

$$\frac{1}{k_{obs}} = \frac{(1 + K_{1,HA}[Hacac]_{enol}) + K_{1,dmso}[dmso]}{(k_2 + k_{3,HA})K_{1,HA}[Hacac]_{enol}} \quad (7b)$$

The addition of H_2O to the sample solutions has both retardation and acceleration effects. The former arises from the competition between H_2O and the incoming $Hacac_{enol}$ because H_2O acts as a base, as does dmso. Retardation was observed for $[Th(acac)_4]$,[9] in which the large Th^{4+} ion is present (ionic radius = 105 pm). The latter effect is caused by the fact that H_2O behaves as a proton acceptor and donor through hydrogen bonding with the nine-co-ordinate adduct.[10] The acceleration effect was observed for $[Hf(acac)_4]$ and $[Zr(acac)_4]$, where the ionic radii of the Hf^{4+} and Zr^{4+} ions are much smaller than that of Th^{4+}. It is interesting that the acceleration and retardation effects of H_2O cancel out in acac exchange in $[Ce(acac)_4]$,[11] in view of the fact that the ionic radius of Ce^{4+} is between those of Zr^{4+} and Th^{4+}. It is inferred that the effect of added H_2O on the rate appears to be related to the ionic radius of the central metal ion.

The existence of a proton-transfer process in the rate-determining step may be substantiated by studies of the deuterium isotope effect on the rate by using Dacac (DA). The kinetic isotope values ($= k_{obs}^H/k_{obs}^D$) measured in this study are comparable to those for $[Hf(acac)_4]$[10] but much smaller than those (*ca.* 9) for $[Th(acac)_4]$.[9] The difference is attributed to the relative magnitudes of k_2^H and k_{3HA}. According to equation (5a), the kinetic isotope effect is given by the ratio $(k_2^H + k_{3,HA})/(k_2^D + k_{3,DA})$, which is equal to $(k_2^H + k_{3,HA})/(k_2^D + k_{3,HA})$ because $k_{3,DA}$ and $K_{1,DA}$ are almost the same as $k_{3,HA}$ and $K_{1,HA}$, respectively. The rate constant k_2^D is that for the proton-transfer process when Dacac is used in place of Hacac. The magnitude of the kinetic isotope effect depends on relative magnitudes of k_2^H ($= k_2$) and $k_{3,HA}$, *i.e.* as the contribution of $k_{3,HA}$ to k_{obs} increases, the kinetic isotope effect decreases. Since $[M(acac)_4]$ complexes with the smaller metal ions form more unstable nine-co-ordinate adducts, the contribution of $k_{3,HA}$ is expected to be greater. It is reasonable, therefore, that the kinetic isotopic values are in the order $[Hf(acac)_4] \approx [Zr(acac)_4] < [Ce(acac)_4] < [Th(acac)_4]$ because the ionic radii are in the order $Hf^{4+} \approx Zr^{4+} < Ce^{4+} < Th^{4+}$.

Conclusion

The ionic radius of the central metal ion has essentially no effect on the mechanism of acac exchange in [M(acac)$_4$] (M = Hf^{4+}, Zr^{4+}, Ce^{4+}, U^{4+} or Th^{4+}). In organic solvents the exchange reaction is initiated by the formation of a nine-co-ordinate adduct [M(acac)$_4$(Hacac)], followed by two parallel rate-determining steps. One step is the proton transfer from Hacac to acac in [M(acac)$_4$(Hacac)] and the other is the ring-opening of acac in the adduct. The ring-opening step plays a more important role in the exchange reaction the smaller the ionic radius of the central metal ion. The significant contribution of the ring-opening step results in a relatively small kinetic isotopic effect for the ligand-exchange reaction in [M(acac)$_4$]. The effect of added H_2O on the rate is related to the ionic radius of the central metal ion.

Acknowledgements

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