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Deuterium Isotope Effect on the Rate of Ligand Exchange between Tetrakis(acetylacetonato)thorium(IV) and Free Acetylacetone in CD_3CN

Naoshi Fujiwara,*,† Tomoe Nakagawa, Hiroshi Tomiyasu, and Hiroshi Fukutomi††
Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, O-okayama 2-12-1, Meguro-ku, Tokyo 152

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Synopsis. A deuterium isotope effect on the rate of acetylacetonate exchange between tetrakis(acetylacetonato)thorium(IV), $Th(acac)_4$, and free acetylacetone in CD_3CN has been examined by means of ^1H NMR technique. The second-order rate constant, k, which is expressed as a function of the observed first-order rate constant, k_{obsd}, and the concentration of acetylacetone in the enol form, $[acetylacetone]_{enol}$, by $k=k_{obsd}/[acetylacetone]_{enol}$ was determined for the reaction of deuterated acetylacetone, Dacac, as well as undeuterated acetylacetone, Hacac. The ratio of second-order rate constants for Hacac and Dacac, k_H/k_D, was approximately 9. This large deuterium isotope effect strongly supports a mechanism proposed in a previous paper that the proton transfer process is the rate determining step of the whole reaction.

Much interest has been concerned with respect to ligand exchange reactions in various acetylacetonato complexes.[1-9] In an earlier paper, we reported the study on the kinetics of acac exchange in $Th(acac)_4$ and proposed a mechanism passing through a nine coordinate intermediate, $Th(acac)_4$···Hacac, where Hacac in the enol form coordinated as a unidentate ligand and a proton transferred from Hacac to one of four acac's at the rate determining step.[2]

This paper presents results of the deuterium isotope effect of the acac exchange in $Th(acac)_4$ in order to clarify the above mechanism.

Experimental

Materials. The complex $Th(acac)_4$ was synthesized by the method reported previously.[2] Acetylacetone was deuterated by the reported method.[7] The deuteration of the methine proton in coordinated acac was carried out by the following procedure: $Th(acac)_4$ (0.2 g) and deuterated acetylacetone Dacac (0.5 g) was dissolved in 2 cm^3 of dichloromethane, and the solvent involving Dacac and Hacac was removed by evaporation under reduced pressure, and then the resulted precipitate was dried in vacuo at 100 °C for one day. Acetonitrile-d_3 (Merck Co., Ltd.) was dried over Molecular Sieves 4A (Wako Pure Chemical Ltd.). Dichloromethane (Wako) was dried over anhydrous calcium chloride (Wako) for one day and distilled. Acetylacetone (Wako) and deuterated acetylacetone were dried over anhydrous calcium sulfate and distilled twice before use.

Kinetic Procedure. $Th(acac)_4$, Dacac, and CD_3CN were weighed, and sealed in a 5 mmϕ NMR sample tube. A JEOL JNM FX-100 FT NMR spectrometer equipped with a JNM-VT-3B temperature controller was used for measurements of ^1H NMR spectra. The water content of the reaction mixture was analyzed by the Karl-Fischer titration. The rate constants of the exchange reaction were determined from the line shape analysis of methine proton signals by using the two-site model.[2]

Results

Deuterium Isotope Effect on the Acac Exchange in $Th(acac)_4$. The ^1H NMR spectra of methine protons for the mixture of $Th(acac)_4$ and Hacac, and their deuterated species in CD_3CN were measured at various temperatures (Fig. 1). The deuterated fraction of acetylacetone was determined to be 86% based on the ratio of peak areas of methine and methyl protons. The signals of coordinated acac (upper field) and that of free $Hacac_{enol}$ (lower field) were observed separately at 0 °C. However, two signals tended to coalesce as the temperature was raised. Though the difference in the chemical shifts of the methine proton signals between Dacac and $Th(acac)_4$ is less than that between Hacac and $Th(acac)_4$, the coalescence temperature of 28 °C was significantly higher than that of 12 °C for the exchange between undeuterated $Th(acac)_4$ and $Hacac_{enol}$.[2] This clearly indicates that the exchange

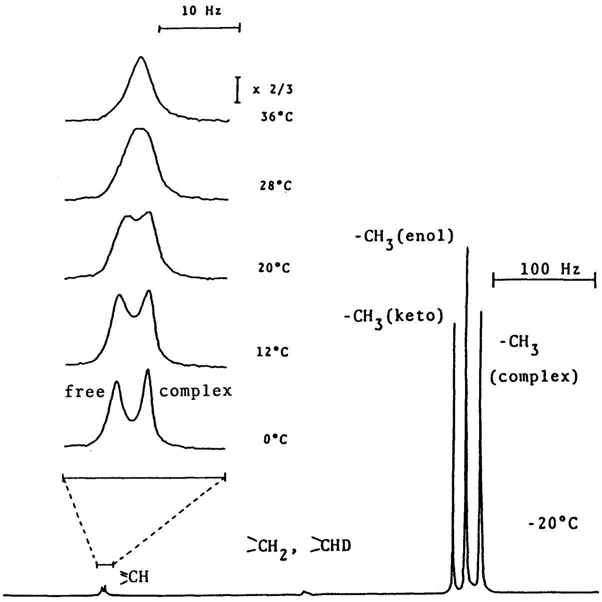

Fig. 1. ^1H NMR spectrum of the mixture of $Th(acac)_4$ and deuterated acetylacetone in CD_3CN, and the change of methine proton signals with temperatures. $[Th(acac)_4]=0.106$ mol kg^{-1}, $[Hacac]_{total}$ (deuterated fraction: 86%)=0.690 mol kg^{-1}, and $[H_2O]=0.08$ mol kg^{-1}. The observed first-order rate constant k_{obsd} was determined at various temperatures as follows.

T/°C	12.0	20.0	28.0	36.0
k_{obsd}/s^{-1}	17.2	24.0	33.4	43.0

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† Present address: Department of Anesthesiology, School of Medicine, Niigata University, Asahimachi-dori 1-757, Niigata 951.

†† Present address: Department of Chemistry, Faculty of Science, Okayama University, Tushimanaka, Okayama 700.

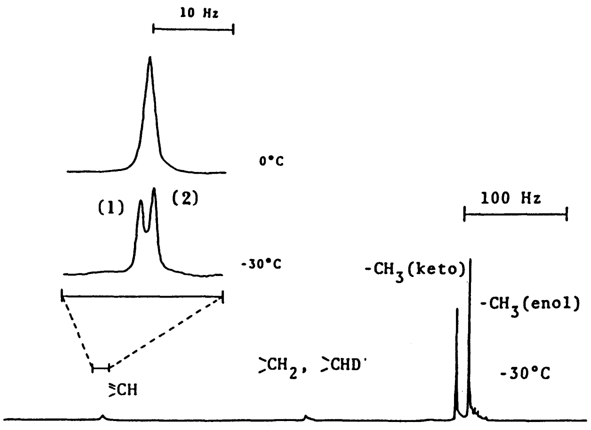
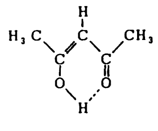


Fig. 2. ^{1}H NMR spectrum of deuterated acetylacetone in CD_3CN at −30 °C. The expanded signals of methine proton at −30 and 0 °C are also shown. $[\mathrm{Hacac}]_{\mathrm{tatal}}$ (deuterated fraction: 55%)=0.667 mol kg^{-1} and $[H_2O]$=0.06 mol kg^{-1}.

reaction in the deuterated system is much slower than in the undeuterated one.

Acac Exchange between Hacac and Dacac. The NMR spectra of the methine proton of deuterated $\mathrm{Hacac}_{\mathrm{enol}}$ (deuterated fraction 55%) in the absence of $\mathrm{Th(acac)_4}$ are shown in Fig. 2. Two signals, which were observed at −30 °C, coalesced to a single peak at 0 °C. Four types of isotope isomers exist in incompletely deuterated $\mathrm{Hacac}_{\mathrm{enol}}$ as written below.



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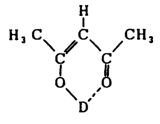

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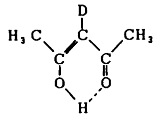

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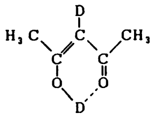

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Among these isomers, only **1** and **2** give the methine proton signals. On the basis of the signal intensity, the peaks in upper and lower fields are assigned as the signals of **2** and **1**, respectively. The exchange rate between **1** and **2** was calculated by use of the two-site model. The reciprocal values of life time for **1**, which correspond to the first-order rate constant for exchange of two methine protons, were determined to be 3.63, 1.97, and 0.82 s^{-1} at 0, −10, and −20 °C, respectively. Because of the very narrow splitting between the signals of **1** and **2**, the singls coalesced at 0 °C, although the exchange rate was comparable with that of acac exchange between $\mathrm{Th(acac)_4}$ and $\mathrm{Dacac}_{\mathrm{enol}}$. The broadening of the methine proton signals due to the exchange between **1** and **2**, however, was taken into account for the calculation of the exchange rates between $\mathrm{Th(acac)_4}$ and $\mathrm{Dacac}_{\mathrm{enol}}$.

Discussion

In the previous paper,[2] the rate of the exchange between $\mathrm{Th(acac)_4}$ and free Hacac was found to be first order in both $[\mathrm{Th(acac)_4}]$ and $[\mathrm{Hacac}]_{\mathrm{enol}}$. Since the same rate law is expected for the exchange between $\mathrm{Th(acac)_4}$ and Dacac, the observed first-order rate constant, k_{obsd}, is expressed by Eq. 1.

$$k_{\mathrm{obsd}}=k[\mathrm{Dacac}]_{\mathrm{enol}} \qquad (1)$$

where k is the second-order rate constant and $\mathrm{Dacac}_{\mathrm{enol}}$ consists of the four isotope isomers **1**, **2**, **3**, and **4** in the incompletely deuterated system. Therefore, Eq. 1 yields

$$k_{\mathrm{obsd}}=k_1[\mathbf{1}]+k_2[\mathbf{2}]+k_3[\mathbf{3}]+k_4[\mathbf{4}] \qquad (2)$$

where k_1, k_2, k_3, and k_4 are the second-order rate constants for **1**, **2**, **3**, and **4**, respectively.

It is reasonable to assume that $k_1=k_3(=k_{\mathrm{H}})$ and $k_2=k_4=(k_{\mathrm{D}})$, because the primary isotope effects due to O-H and O-D groups are of essential importance for the exchange rate. Then, Eq. 2 is written by

$$k_{\mathrm{obsd}}=k_{\mathrm{H}}([\mathbf{1}]+[\mathbf{3}])+k_{\mathrm{D}}([\mathbf{2}]+[\mathbf{4}]). \qquad (3)$$

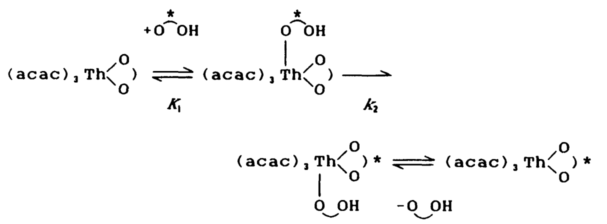
The values of k_{H} were determined previously[2] and the concentrations $[\mathbf{1}]+[\mathbf{3}]$ and $[\mathbf{2}]+[\mathbf{4}]$ were calculated from the NMR signal intensity. These data along with Eq. 3 give the values of k_{D}, which are listed in Table 1. The ratio $k_{\mathrm{H}}/k_{\mathrm{D}}$ is about 9. This value is close to the maximum of the kinetic isotope effect, which is estimated from the difference in the zero-point energy of O-H and O-D bonds in Hacac and Dacac, respectively.[8] The deuterium isotope effects for acac exchange reactions were reported in a variety of complexes, $\mathrm{M^{III}}$=$\mathrm{Cr^{III}}$, $\mathrm{Co^{III}}$, $\mathrm{Rh^{III}}$, $\mathrm{Fe^{III}}$, and $\mathrm{V^{III}}$, and $\mathrm{VO(acac)_2}$.[3–7] The small isotope effects observed in these reactions were consistent with mechanisms that the addition of free Hacac to the complexes or the dissociation of acac from the complexes, which preceded the proton transfer step, substantially governed the whole reaction rates. An only exception was recently reported for the acac exchange in $\mathrm{Sc(acac)_3}$, which revealed the considerably large isotope effect ($k_1^{\mathrm{H}}/k_1^{\mathrm{D}}=5$, where k_1 was related to k_{obsd} as $k_{\mathrm{obsd}}=k_1\,[\mathrm{acac}]_{\mathrm{enol}}$).[8] In the latter case, a role of the proton transfer step was consider to be particular importance for the exchange rate.

In the present study, the deuterium isotope effect is largest of all acac exchange reactions ever studied and $k_{\mathrm{H}}/k_{\mathrm{D}}$ is closed the maximum value. Morever, the rate of acac exchange between $\mathrm{Th(acac)_4}$ and Dacac is comparable with that between Hacac and Dacac. These facts strongly supports the following

Table 1. Deuterium Isotope Effect on the Second-Order Rate Constant k for the acac Exchange Reaction in $\mathrm{Th(acac)_4}$ in CD_3CN

T/°C	k_{H}/s^{-1} mol^{-1} kg	k_{D}/s^{-1} mol^{-1} kg	$k_{\mathrm{H}}/k_{\mathrm{D}}$
12	184	18.6	9.9
20	246	27.6	8.9
28	351	37.0	9.5

reaction mechanism proposed in the previous paper,[2)]



where O⌒O and O⌒OH represent acac and $\mathrm{Hacac_{enol}}$, respectively and proton transfer process (k_2 path) determined the exchange rate.

A similar mechanism was also proposed for the tta (tta=2-thenoyltrifluoroacetonate) exchange in $\mathrm{Th(tta)_4}$.[10)] In this case, the addition of DMSO (dimethyl sulfoxide) to the complex forming $\mathrm{Th(tta)_4}$···dmso was directly observed by ^{1}H NMR measurements and the exchange of dmso was found to be extremely fast (10^2 s^{-1} at −92 °C). This fact is consistent with the above mechanism that K_1 path is in fast equilibrium prior to the proton transfer.

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