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# $^1$H NMR STUDY OF THE LIGAND EXCHANGE REACTION IN TETRAKIS-(2,4-PENTANEDIONATO)THORIUM(IV)

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The rate of ligand exchange in tetrakis(2,4-pentanedionato)thorium(IV) was first measured by the $^1$H NMR line-shape analysis. The observed first-order rate constant is proportional to the concentration of free 2,4-pentanedione in enol form and the exchange is retarded by the addition of bases such as dimethyl sulfoxide and N,N-dimethylformamide.

Tetrakis(2,4-pentanedionato)thorium(IV), Th(acac)$_4$, where hereafter the common name of the ligand, i.e. acetylacetonate (acac) will be used, has been known as one of the eight-coordinate complexes having a square antiprismatic structure, which is seen in the complexes, Zr(acac)$_4$, Hf(acac)$_4$ and U(acac)$_4$.$^{1)}$ Little is known about the kinetics of the ligand substitution in Th(IV) complexes. Adams and Larsen$^{2)}$ reported that the rate of acac exchange in benzene was too fast to measure by the $^1$H NMR method. However, our recent study found that the rate of exchange of acac between Th(acac)$_4$ and Hacac in chloroform can be measured by $^1$H NMR in the temperature range from -24°C to 0°C.

The reaction mixture of Th(acac)$_4$ and Hacac in chloroform-d gives three methyl proton signals at -24°C. The assignment of these signals was made by changing the compositions of Th(acac)$_4$ and Hacac. The result shown in Fig.1 is consistent with that reported by Pinnavaia and Fay.$^{3)}$ As the temperature increases, coalescence of the methyl proton signal of Th(acac)$_4$ and that of free Hacac in enol form takes place, while the signal of Hacac in keto form is kept unchanged (Fig.1). The ligand exchange reaction can be written as follows.

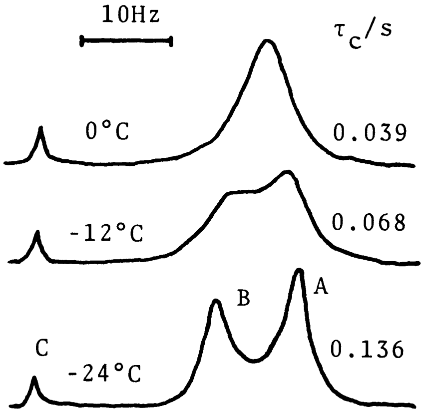

Fig.1. $^1$H NMR spectra of methyl protons at various temperatures; A, Th(acac)$_4$; B, Hacac(enol); C, Hacac(keto); [Hacac]=0.32 mol kg$^{-1}$, [Th(acac)$_4$]=0.082 mol kg$^{-1}$, in chloroform-d.

$$\mathrm{Th(acac)_4 + Hacac(enol)^* \rightleftharpoons Th(acac)_3(acac)^* + Hacac(enol)} \qquad (1)$$

The first-order rate constant, $k_{ex}$($=\tau_c^{-1}$, where $\tau_c$ is the life time of the coordination site), was determined from the line-shape analysis by using the two-site model for the methyl proton signals of $Th(acac)_4$ and Hacac in enol form. The plot of $k_{ex}$ vs. [Hacac(enol)] is linear passing through the origin (Fig.2). The rate law is given by eq.(2).

$$4k_{ex} = k[\mathrm{Hacac(enol)}] = \mathrm{rate}/[\mathrm{Th(acac)_4}] \qquad (2)$$

The second-order rate constants, k, are $(3.7\pm0.2)\times10^2\ s^{-1}mol^{-1}kg$ at 0°C and $(1.6\pm0.1)\times10^2\ s^{-1}mol^{-1}kg$ at -16°C.

The retardation effect on the ligand exchange was observed when the bases such as dimethyl sulfoxide and N,N-dimethylformamide were added to the reaction mixture. This kinetic behavior is very similar to the ligand exchange in $U(fod)_4$ (fod=1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-heptanedionate).[4] Folcher et al. proposed that the ligand exchange in $U(fod)_4$ occurs via a nine-coordinate intermediate. Several nine-coordinate Th(IV) complexes were isolated by Bok et al.,[5] e.g., $Th(TTA)_4TOPO$, $Th(TTA)_4TBP$, where TTA, TOPO and TBP are 2-thenoyltrifluoroacetonate, trioctylphosphine oxide and tributyl phosphate, respectively. On the basis of these facts, it is assumed that a nine-coordinate species is formed as an intermediate of the ligand exchange process between $Th(acac)_4$ and Hacac. More detailed kinetic experiments are in progress to clarify the exchange mechanism.

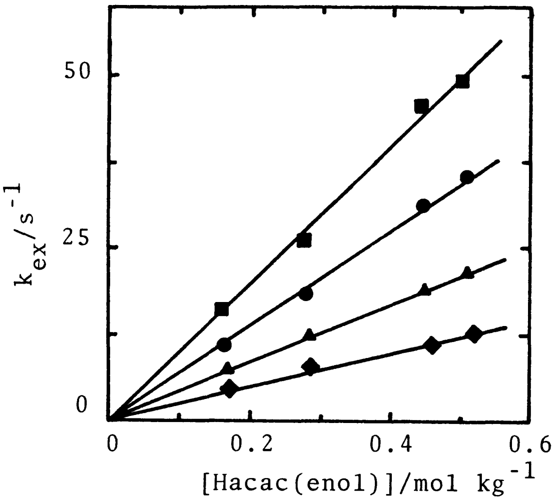

Fig.2. Plot of $k_{ex}$ vs. [Hacac(enol)] at 0°C (■), -8°C (●), -16°C (▲) and -24°C (◆); $[Th(acac)_4]=0.082$ mol $kg^{-1}$, in chloroform-d.

References

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