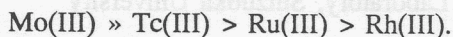


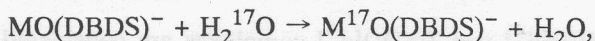
$$R = k_1 [\text{Tc}(\text{acac})_3] \quad (3)$$

where k_1 is the observed first-order rate constant. In the second transition series of tris(acetylacetonato)metal(III) complexes, the k_1 value decreases in the order



In the ligand exchange reaction of $\text{Tc}(\text{acac})_3$, a kinetic parameter ΔS^\ddagger is negative. A similar feature was found in the exchange reaction of pyridine on $\text{trans-}[\text{MO}_2(\text{py})_4]^+$ ($\text{M} = \text{Tc}$ or Re), which was monitored by $^1\text{H-NMR}$ [4]. These reactions are considered to proceed by a dissociative mechanism and the ratio of the reaction rate constants, $k_{\text{Tc}}/k_{\text{Re}}$, has large value.

On the other hand, an example was found that the exchange proceeds in an associative mode[5]. In the oxygen exchange reaction of square-pyramidal monooxo-technetium(V) and -rhenium(V) complexes with N,N' -bis(mercaptoacetyl)butane-1,4-diamine(DBDS),



both complexes are stable toward ligand substitution in the aqueous DMSO solution. However, the slow exchange was recognized on addition of sodium methoxide as a catalyst. The reaction was independent of $[\text{H}_2\text{O}]$ and depends on $[\text{CH}_3\text{O}^-]$. In these systems, the kinetic parameter ΔS^\ddagger was positive, showing a larger structural *trans* effect.

2. Ligand substitution reactions of technetium complexes

In the course of the reduction of pertechnetate with concentrated hydrochloric acid, TcOCl_4^- ion can easily be formed. Furthermore, recent investigation revealed that TcNCl_4^- ion also formed in the presence of sodium azide. These complexes can be used for the syntheses of Tc(V) and Tc(VI) complexes possessing oxo and nitrido cores, respectively, as starting materials. The reduction of pertechnetate with hydrochloric acid finally yields the tetravalent state and no further reduction to trivalent state takes place. Consequently, the trivalent technetium complex has usually been synthesized by the reduction of pertechnetate with an appropriate reductant in the presence of a desired ligand.

Recently, we found that hexakis(thiourea)technetium(III) (or chloropentakis(thiourea)technetium(III)) which is easily formed by the reaction of pertechnetate and thiourea in the presence of hydrochloric acid is suitable for the syntheses of trivalent technetium(III) complexes as a starting material. In fact, tris(β -