Oxygen Atom Transfer Catalytic Property of Oxorhenium(V) Complex with 2-Methylquinolin-8-ylamide and Tetrachlorocatecholate

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New oxorhenium(V) complex was prepared and characterized by an X-ray crystal analysis. The complex showed characteristic releasing property of monodentate ligand and high oxygen atom transfer catalytic activity from 2,6-lutidine-*N*-oxide to PPh_3.

Some oxorhenium(V) complexes have received much attention from the viewpoint of oxygen atom transfer (OAT) catalyst.[1] The redox system of Re(V/VII) in OAT reaction is isoelectronic with the redox system between the +IV (d^2) and +VI (d^0) oxidation state of active site of molybdenum or tungsten enzymes, which are known for good OAT catalysts in biological systems.[2] Since the OAT catalytic reaction needs a vacant site on the metal center, which can act as a reaction field, the study of stereochemistry and reactivity of oxorhenium(V) complexes is important for development of excellent OAT catalysts. In our previous work, it revealed that the chloro complex $[ReOCl_2(Hamq)(PPh_3)]$ (**1**) (H_2amq = 8-amino-2-methylquinoline) has an easy releasing property of the weakly coordinated ligand PPh_3 and show the OAT catalytic property by using a vacant site.[3] However, the lifetime of catalyst **1** was only 10 cycles and decomposition to perrhenate(VII) was observed.[4] In this work, the tetrachlorocatecholato (Cl_4cat^{2-}) complex $[ReO(Cl_4cat)(Hamq)(PPh_3)]$ (**2**) was synthesized for stabilizing the complex by the chelate effect. The structure of **2** was determined by X-ray diffraction and OAT reaction from 2,6-lutidine-*N*-oxide (luO) to PPh_3 by **2** was investigated. It was elucidated that complex **2** showed high catalytic activity.

To a solution containing H_2Cl_4cat in $(CH_3)_2CO/H_2O$ mixed solvent was added **1** and stirred. After concentrating this solution until a precipitate appeared, the precipitated complex **2** was collected.[5] An X-ray crystal analysis for **2** revealed the presence of a complex molecule and an $(CH_3)_2CO$ molecule.[6] The coordination geometry around the Re atom is a distorted octahedral with three O atoms of the oxo and catecholate ligands, two N atoms of the quinolinylamide ligand, and one P atom of the PPh_3 ligand (Figure 1). The Re1–N1 distance is somewhat longer than that in **1** (2.165(4) Å) because of the *trans* influence of PPh_3. Though the Re1–O1 distance is shorter than that in **1** (1.724(4) Å), it is normal as the double bond in oxorhenium(V) complexes.[7] The Re1–O3 distance is longer than the Re1–O2 distance, and it lies at the longest value of the range found for the Re–O (catecholate or phenolate) distances (1.96–2.10 Å).[7] This long bond distance would exhibit the *trans* influence of the Re1–N2 (amide) bond.

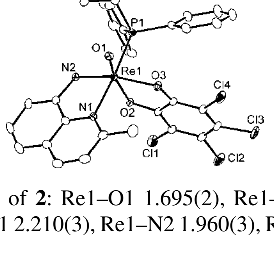


Figure 1. Structure of **2**: Re1–O1 1.695(2), Re1–O2 2.026(2), Re1–O3 2.126(3), Re1–N1 2.210(3), Re1–N2 1.960(3), Re1–P1 2.4557(9) Å.

The UV–vis absorption spectrum of **2** showed concentration dependence as in the case of **1**. The increase of the peak intensity at 402 and 816 nm with increasing the concentration of **2** was observed. When the excess amount of PPh_3 was added to the solution of **2** (1.0×10^{-4} mol dm^{-3}), a similar spectral changing is observed. Therefore, the concentration dependence would indicate the release or bonding of PPh_3. Since **2** releases the monodentate ligand PPh_3 and has a vacant site in solution, the OAT catalytic reactivity from luO to PPh_3 was investigated. The OAT catalytic reaction of **2** was monitored by UV–vis absorption spectra in CH_2Cl_2. The progression of reaction was obtained by converting absorbance to luO concentration according to eq 1. The control experiments of the reaction between luO and PPh_3 without **2** showed no reaction. Addition of oxygen donor luO, in the absence of PPh_3, the solution of **2** turned from orange to deep reddish-purple, which have a new intense band at 489 nm. The active state seems to be $[ReO_2(Cl_4cat)(Hamq)]$, since the spectroscopic character is in agreement with that of dioxorhenium(VII) complexes.[8] The absorbance–time profile showed decomposition of the active state dioxorhenium(VII) complex under the condition of the solvent containing H_2O and absence of PPh_3. On the other hand, the catalysis proceeds normally as long as PPh_3 remains. This fact indicates that the recycling of **2** between its resting and active states prevents its decomposition during the catalytic stage. Namely, the reaction rate of dioxo active states with PPh_3 is much faster than that of dioxo decomposition as long as enough PPh_3 remains.

$$[\mathrm{luO}]_t = [\mathrm{luO}]_0 \frac{\mathrm{Abs}_t - \mathrm{Abs}_\infty}{\mathrm{Abs}_0 - \mathrm{Abs}_\infty} \quad (1)$$

The initial rates are obtained from the concentration-time curve fitting with a least-squares program by using the data from start to 60 s later (Figure S1).[9] When the initial concentrations of **2** were varied and those of luO and PPh_3 were fixed, the increase of initial rates was observed with increase of the concentration of **2**. Since the slope of the log–log plot was 1 (Figure 2a), the reaction order of concentration of **2** is estimated to 1. Similarly, from the slope of the log–log plot (Figures 2b and 2c), the reaction order of concentration of luO is estimated to 1 and that of PPh_3 is −1. Consequently, the initial rate equation is determined as eq 2. Its form is further confirmed by a plot of all the values of v_0 against the composite concentration variable. The data are in agreement with this model (Figure 2d), and least-square fitting affords $k_c = 1.8\ \mathrm{s}^{-1}$ at 23 °C in CH_2Cl_2. This catalytic activity of **2** is comparable to $[MeReO(mtp)(PPh_3)]$ (H_2mtp = 2-

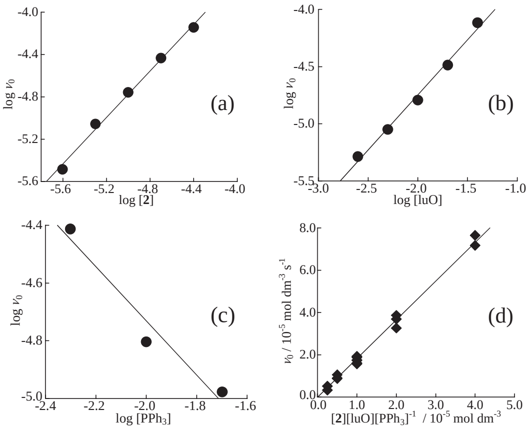


Figure 2. The initial rates of reaction depend on each concentration, as shown on log–log scales: (a), [**2**] was varied with 0.010 M of luO and PPh_3; (b), luO was varied with 0.010 mM of **2** and 0.010 M of PPh_3; (c), PPh_3 was varied with 0.010 mM of **2** and 0.010 M of luO. (d) Displays the initial rates of reaction dependence on the combined concentration variable, as in eq 2.

(mercaptomethyl)thiophenol), which is a typical methylated oxorhenium(V) complex with OAT catalytic property reported by Espenson et al.[10] Such a high reactivity is rare example for non-methylated oxorhenium(V) complexes.

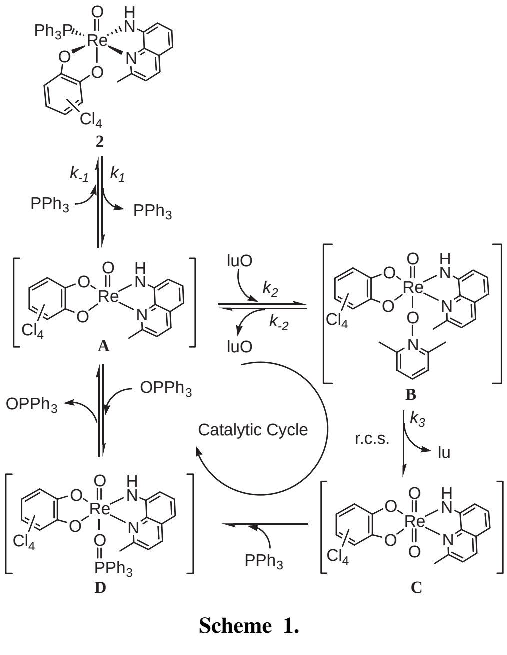
$$v_0 = k_c \frac{[\mathbf{2}][\mathrm{luO}]}{[\mathrm{PPh_3}]} \tag{2}$$

From the results of the present measurements, the reaction cycle is supposed to Scheme 1. In brief, it comprises the following steps: (1) **2** releases the PPh_3 ligand and forms the five-coordinated intermediate **A**; (2) **A** and luO form the luO coordinated intermediate **B**; (3) lu is released from **B**, to form the dioxo intermediate **C**; (4) **C** reacts with PPh_3 quite rapidly and forms **D**, without an influence on the rate; (5) $OPPh_3$ is released from **D** and **A** is regenerated. Since $OPPh_3$ is absent at an initial step, the rate law for Scheme 1 is derived from two equations, $[\mathbf{A}] = (k_1[\mathbf{2}] + k_{-2}[\mathbf{B}])/(k_{-1}[\mathrm{PPh_3}] + k_2[\mathrm{luO}])$ and $[\mathbf{B}] = k_2[\mathbf{A}][\mathrm{luO}]/(k_{-2} + k_3)$. Eq 3 is obtained by solving these equations. If the third step is assumed to the rate controlling step (r.c.s.) as with the literature,[10] the reaction rate v_0 is equal to $k_3[\mathbf{B}]$. To attain correspondence between eqs 2 and 3, the luO denominator term in eq 3 must be negligible, so that the equation simplifies to the first form in eq 4. Since the rate constant in r.c.s. (k_3) is much smaller than k_{-2}, the equation is further simplified to the final form in eq 4.

$$k_3[\mathbf{B}] = \frac{k_1k_2k_3[\mathbf{2}][\mathrm{luO}]}{(k_{-1}k_{-2} + k_{-1}k_3)[\mathrm{PPh_3}] + k_2k_3[\mathrm{luO}]} \tag{3}$$

$$v_0 = \frac{k_1k_2k_3[\mathbf{2}][\mathrm{luO}]}{(k_{-1}k_{-2} + k_{-1}k_3)[\mathrm{PPh_3}]} \tag{4}$$

$$\xrightarrow{(k_3 \ll k_{-2})} = \frac{k_1k_2k_3[\mathbf{2}][\mathrm{luO}]}{k_{-1}k_{-2}[\mathrm{PPh_3}]} = K_1K_2k_3\frac{[\mathbf{2}][\mathrm{luO}]}{[\mathrm{PPh_3}]}$$



Scheme 1.

The rate equations, rate constants, and catalytic cycle schemes of the OAT catalytic property in **2** were investigated. As a result of the introducing didentate catecholate derivatives, the stability of the catalyst was significantly improved. That is, the total turnover number of **2** was at least 400 times greater than that of **1**. Furthermore, it was revealed that the OAT catalytic reaction rate of **2** is obviously much faster than that of **1**, which was monitored by ^{1}H NMR spectra (Figure S2).[9] The reaction rate of **2** was comparable with that of the methylated oxorhenium(V) complex.

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References and Notes

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6 Crystal data for **2**: $C_{37}H_{30}Cl_4N_2O_4PRe = 925.65$, triclinic, $P\bar{1}$, $a = 9.244(3)$, $b = 11.851(8)$, $c = 17.204(5)$ Å, $\alpha = 77.653(5)$, $\beta = 84.442(8)$, $\gamma = 84.711(7)°$, $V = 1827.5(9)$ Å^3, $Z = 2$, $T = 296$ K, $D_{\mathrm{calcd}} = 1.682$ g cm^{-3}, R (R_w) = 0.034 (0.099), GOF = 0.955; CCDC 600497.
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