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Aerobic Oxidation of Methyl *p*-Tolyl Sulfide Catalyzed by a Remarkably Labile Heteroscorpionate Ru(II)−Aqua Complex, *fac*-$[Ru^{II}(H_2O)(dpp)(tppm)]^{2+}$

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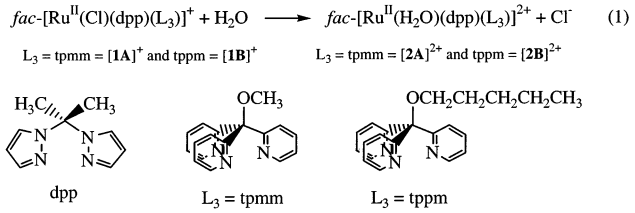
Catalytic and stoichiometric oxidations of sulfide by peroxides, periodate salts, enzymatic systems, and transition-metal-based oxidants are important from biochemical,[1] environmental,[2] and industrial perspectives.[3] There are only a few examples of transition-metal-based catalysts using molecular oxygen as the oxidant because sulfide has been well-known for many years as a poor ligand[4] and is, therefore, not able to displace peroxide from an inner-sphere peroxide catalysts. Its sulfoxide analogue, on the other hand, is not a good leaving group after binding to a catalyst that contains an oxygen donor ligand. To avoid suffering from a very slow oxidation rate or no catalytic reactivity, transition-metal-based catalysts must be used together with highly reactive peroxides such as H_2O_2 and *tert*-BuO_2H as the ultimate oxidants[5] or have a highly reactive peroxide involved as an intermediate, sometimes generated via an outer-sphere electron-transfer pathway.[6]

We previously reported that the aerobic oxidation of cyclohexene catalyzed by *cis*-$[Ru^{II}(H_2O)(bpy)_2(PR_3)]^{2+}$ (bpy = 2,2′-bipyridine and PR_3 = tertiary phosphine) involved a putative *cis*-$[Ru^{IV}(bpy)_2(PR_3)(O)]^{2+}$ intermediate without the formation of H_2O_2.[7a] We recently reported the remarkable heteroscorpionate ligand effect on rate enhancement (1.9×10^7) of ligand substitution kinetics for *fac*-$[Ru^{II}(H_2O)(dpp)(tpmm)]^{2+}$ (dpp = di(pyrazol-1-yl)propane and tpmm = tris(pyrid-2-yl)methoxymethane).[8]



We now report a unique combination of the two studies in which the low-oxidation state heteroscorpionate $Ru^{II}-H_2O^{2+}$ complex having a remarkable steric ligand effect is used as a catalyst for aerobic oxidation of methyl *p*-tolyl sulfide to methyl *p*-tolyl sulfoxide. This novel reactivity is the first documented example of aerobic sulfide oxidation catalyzed by a transition-metal complex without the formation of a highly reactive peroxide as an intermediate. Remarkably, this aerobic oxidation of sulfide occurs due primarily to the steric effect of the heteroscorpionate dpp ligand. The X-ray crystal structure of [**2A**]$(PF_6)_2$ with crystals grown by a slow diffusion of $CH_3C(O)CH_3$ out of a 1:1 (v/v) H_2O:$CH_3C(O)CH_3$ solution is shown in Figure 1.

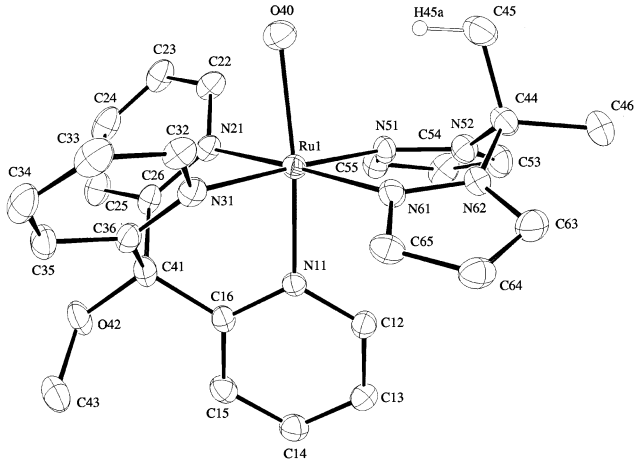


Figure 1. ORTEP diagram of the *fac*-$[Ru^{II}(H_2O)(dpp)(tpmm)]^{2+}$ cation.

Aerobic oxidation of methyl *p*-tolyl sulfide catalyzed by [**2B**]$(PF_6)_2$ in 1,2-dichlorobenzene (ODCB = *o*-dichlorobenzene) at 25.0 ± 0.1 °C was monitored by $GC^{I}-MS$.[9]

This aerobic sulfide oxidation study is reminiscent of those by Riley,[6a−b] Mestroni,[6c] Fergusson,[6d] Espenson,[5a] Kagan,[5b] and Seraglia.[5c] However, these reactions require vigorous conditions and are known to occur only when highly reactive peroxides such as H_2O_2 or *tert*-BuO_2 are involved as the intermediate or are used as the oxidants. For example, alkylarylsulfides were catalytically oxidized by *cis*- or *trans*-$[Ru^{II}(X)_2(DMSO)_4]$ (X = Cl or Br),[6a] *fac*- or *mer*-$[Ru^{II}(Br)_2(THT)(BEPS)]$ (THT = tetrahydrothiophene and BEPS = bis(3-(ethylsulfinyl)propyl)-sulfide),[6b] *trans*-$[Ru^{III}(Cl)_4(DMSO)_2]^-$, or *mer*-$[Ru^{III}(Cl)_3(DMSO)_3]$[6c] with the formation of H_2O_2 as the intermediate. In the catalytic oxidations of alkylarylsulfides and chiral sulfides, $[Re^{VII}(CH_3)(O)_3]$[5a] and $[Ti^{VI}(i\text{-}OC_3H_7)_4]$,[5b] $[V^{V}(O)(i\text{-}OC_3H_7)_3]$,[5c] $[Mo^{VI}(O)_2(acac)]$ (acac = acetylacetonato), or $[Mo^{VI}(O)(O_2)_2]$[5c] must be used with H_2O_2 and *tert*-BuO_2H as the oxidants, respectively.

In addition, our sulfide oxidation study is reminiscent of those by James[10a] and Meyer.[10b] However, the aerobic sulfide oxidation catalyzed by Ru(VI)−dioxo porphyrin reported by James and co-workers was suppressed after 20 min with a turnover of ~5 because the more labile O-bound sulfoxide $Ru^{II}-(OSR_2)_2^{2+}$ complex underwent isomerization to form the substitutionally inert S-bound sulfoxide $Ru^{II}(S(O)R_2)_2^{2+}$ complex which terminated the catalytic process. This is a typical problem for unhindered transition-metal catalysts. Although the sulfide oxidation by *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ reported by Meyer had a much faster rate of forming the O-bound sufoxide $Ru^{II}-OSR_2^{2+}$ product and a much slower

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rate of isomerization to the corresponding S-bound $Ru^{II}-S(O)R_2^{2+}$ product, unfortunately, this Ru(IV)−oxo complex did not possess the catalytic reactivity toward thioether oxidation.

In our study, methyl *p*-tolyl sulfide was readily oxidized by [**2B**]-$(PF_6)_2$ to methyl *p*-tolyl sulfoxide. The turnover number was calculated as 53 after a period of 36 h, eq 2.[9]

$$(CH_3)(p\text{-}CH_3C_6H_4)S \xrightarrow[\text{ODCB, } 25.0 \pm 0.1\ ^\circ C]{[O_2]\ (11.4\ \text{psi}),\ [\mathbf{2B}](PF_6)_2\ \text{Cat.}} (CH_3)(p\text{-}CH_3C_6H_4)SO \quad (2)$$

Since the reaction in eq 2 occurs under mild conditions, it presumably proceeds via a mechanism involving the putative *fac*-$[Ru^{IV}(dpp)(O)(tppm)]^{2+}$ intermediate, reminiscent of our aerobic oxidation of cyclohexene catalyzed by *cis*-$[Ru^{II}(H_2O)(bpy)_2(PR_3)]^{2+}$.[7b]

Experimental facts in support of this mechanism are the absence of detected H_2O_2[11] and the reactions in which *fac*-$[Ru^{IV}(dpp)(O)(tpmm)](PF_6)_2$ ([**3A**]$(PF_6)_2$) stoichiometrically oxidizes methyl *p*-tolyl sulfide, 2-propanol, and allyl alcohol to methyl *p*-tolyl sulfoxide, acetone, and glycidol, respectively. The key feature in the proposed mechanism is the extraordinary heteroscorpionate effect of dpp that rapidly extrudes the O-bound sulfoxide ligand before the isomerization can even occur.[9]

[**3A**]$(PF_6)_2$ stoichiometrically reacts with methyl *p*-tolyl sulfide in CH_3CN to form the solvento complex, *fac*-$[Ru^{II}(NCCH_3)(dpp)(tpmm)](PF_6)_2$ ([**4A**]$(PF_6)_2$) and methyl *p*-tolyl sulfoxide as the organic product. The reaction was studied under N_2 by following characteristic change in the absorption spectrum at $\lambda_{max} = 352$ nm as [**3A**]$(PF_6)_2$ was directly converted into [**4A**]$(PF_6)_2$. As shown in the Supporting Information (Figure 2) in the oxidation of methyl *p*-tolyl sulfide by [**3A**]$(PF_6)_2$, the extrusion of methyl *p*-tolyl sulfoxide is too fast for the O-bound $Ru^{II}-OS(CH_3)(p\text{-}CH_3C_6H_4)^{2+}$ intermediate to be even observed. The spectra simply show the direct conversion from [**3A**]$(PF_6)_2$ to [**4A**]$(PF_6)_2$.

Besides sulfide, [**3A**]$(PF_6)_2$ also oxidizes 2-propanol to acetone[12] and epoxidizes allyl alcohol to glycidol, eqs 3−4. The reactions were studied in 0.1 M $HNO_3/NaNO_3$ solution (pH = 2.00) at 25.0 ± 0.1 °C by UV−vis monitoring at $\lambda_{max} = 360$ nm for $[\mathbf{2A}]^{2+}$.

$$[Ru^{IV}(dpp)(O)(tpmm)]^{2+} + (CH_3)_2CHOH \xrightarrow{H_2O} [Ru^{II}(H_2O)(dpp)(tpmm)]^{2+} + (CH_3)_2C{=}O \quad (3)$$

Methyl *p*-tolyl sulfide, acetone, and glycidol were extracted from the reaction solutions with hexane and quantitatively analyzed by

$$[Ru^{IV}(dpp)(O)(tpmm)]^{2+} + CH_2{=}CHCH_2OH \xrightarrow{H_2O} [Ru^{II}(H_2O)(dpp)(tpmm)]^{2+} + \text{glycidol} \quad (4)$$

GC−MS (90−95% yield). In both the catalytic and the stoichiometric oxidations, the number of moles of methyl *p*-tolyl sulfide consumed is equal to the number of moles of methyl *p*-tolyl sulfoxide produced. This mass balance studies show that sulfide is not consumed as sacrificial co-reductant, and the absence of H_2O_2 supports the mechanism reported previuosly.[7b] Representatives of calibration curves and details of product analyses for the catalysis and oxidation of methyl *p*-tolyl sulfide as well as 2-propanol are provided in Supporting Information Figures 5−8 and Table 1.

From the crystallographic data on [**2A**]$(PF_6)_2$, the absence of H_2O_2, the lack of catalytic suppression, and the stoichiometric oxidation of methyl *p*-tolyl sulfide, 2-propanol, and allyl alcohol by [**3A**]$(PF_6)_2$, it can be concluded that the aerobic oxidation of methyl *p*-tolyl sulfide to methyl *p*-tolyl sulfoxide is catalyzed by the heteroscorpionate $Ru^{II}-H_2O^{2+}$ complex possessing a remarkable steric effect of the heteroscorpionate dpp ligand.

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Supporting Information Available: Text containing product analysis and product distribution, Supporting Information Table 1, Supporting Information Figures 1−8 are included (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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