The Reaction of Polypyridyl Ru Mono-oxo Complexes Toward Sulfur Compounds

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Metal oxo complexes have been invoked as models of intermediates in the enzymatic oxidation cycles of cytochrome P-450.[1] Catalytic oxidation reactions when metalloporphyrins used with various oxygen atom transfer reagents for several substrates have been reported.[2] To gain insights into the mechanisms of metal mono-oxo mediated oxidations and possible mechanistic similarities with bioinorganic oxidation catalysts, we and others have investigated the reactions of substrates with novel oxo complexes.[3]

Because of the importance of sulfoxides as intermediates in various reactions and the synthetic versatility of sulfoxides, selective oxidation of organic sulfides to sulfoxides has been the subject of extensive research.[4] One of the simplest methods for oxidation of sulfides to sulfoxides is the use of hydrogen peroxide as an oxidant. Since oxidized products are usually inactive and limited, the oxidation system allows us to investigate the reactivity and the nature of the intermediate clearly. However, the reactivity and mechanism of oxo complexes toward sulfur compounds have not been studied in detail.[5] Recently, Watanabe *et al.* reported that sulfoxidation reactions proceeded either electron transfer or oxygen atom transfer mechanism depending on the use of high-valent intermediates of heme enzymes.[6] Here we describe the oxidation of organic sulfides with polypyridyl ruthenium mono-oxo systems, which show the models of biological oxygenations and dissection of the mechanism.

The oxidants used in the reactions, $[Ru(bpy)_2(py)(O)](ClO_4)_2$ and $[Ru(bpy)_2(p\text{-}tert\text{-}butylpy)(O)](ClO_4)_2$ (bpy is 2,2'-bipyridine; py is pyridine; *p-tert*-butylpy is *para-tert*-butylpyridine), were prepared according to previously known methods.[7] Product analysis in the reactions of the $[Ru^{IV}=O]^{2+}$ complex with organic sulfide by ^1H NMR and GLC using a calibration curve shows the appearance of the corresponding sulfoxide as a sole organic product. Sulfone, as a further oxidized product, was not detected at all under the condition using excess amounts of sulfide.

The spectral changes accompanying the oxidation of cyclic organic sulfide by the $[Ru^{IV}=O]^{2+}$ complex show the rapid formation of an initial O-bound sulfoxide intermediate, which is observed at the wavelength of 488 nm, the subsequent spectra are consistent with solvolysis of the intermediate by CH_3CN to yield the $[Ru^{II}\text{-}NCCH_3]^{2+}$ complex at the wavelength of 442 nm and isomerization of the intermediate to give a S-bound sulfoxide complex having λ_{max} at 393 nm as shown in the UV-vis spectral changes of Figure 1(a). The electronic spectral characteristics of the O-bound sulfoxide intermediate is typical of bipyridine complexes of Ru(II) with oxygen-bound ligands.[8] Deutsch *et al.* have characterized the S-bound $[Ru(tpy)(bpy)(SOMe_2)]^{2+}$ (tpy is 2,2':6',2"-terpyridine) at the wavelength of 412 nm[9] and Roecker *et al.* have also characterized the S-bound $[Ru(bpy)(py)_2(SOMe_2)]^{2+}$ having λ_{max} at 400 nm.[5b] Figure 1(b) also shows that addition of diphenyl sulfide to acetonitrile solutions containing Ru mono-oxo complex in the featureless spectrum in the visible region rapidly affords an O-bound sulfoxide intermediate having λ_{max} at 475 nm. After formed, the O-bound sulfoxide complex undergoes solvolysis to give the $[Ru^{II}\text{-}NCCH_3]^{2+}$ complex at 442 nm but apparently little evidence for the isomerization product of a S-bound sulfoxide in the UV-vis spectral changes.

The sequence of reactions that appears to occur was corroborated with ^1H NMR experiments in which either 0.03 M of pentamethylene sulfide or diphenyl sulfide was added to 0.02 M of the $[Ru^{IV}=O]^{2+}$ complex dissolved in 1 mL CD_3CN. We have already shown that the chemical shift of one of 6'-protons of the bipyridine in complexes of the type of six coordinated $[(bpy)_2(py)Ru^{II}\text{-}X]^{2+}$ complexes that is the nearest to X is shifted furthest downfield. The peak is affected by the nature of X and also indicates the presence of different ligand bound to Ru(II).[5b,10] For pentamethylene sulfide, the rapid formation of an O-bound complex having a characteristic of 6'-proton chemical shift at 9.33 ppm was observed shown in Figure 2(a)-①. After a much longer time scale, both the solvolyzed product $[Ru^{II}\text{-}NCCD_3]^{2+}$ at 9.42 ppm and the isomerized S-bound complex at 10.3 ppm in a much larger amount are detected in the part of ^1H NMR spectrum of Figure 2(a)-②. In the case of diphenyl sulfide, rapid formation of the O-bound complex at 9.00 ppm and the S-bound complex at 10.34 ppm were observed with the solvolyzed product at 9.42 ppm in the ^1H NMR spectrum of Figure 2(b). After 24 hrs, only solvolyzed complex, $[Ru^{II}\text{-}NCCD_3]^{2+}$, at 9.42 ppm is detected as a sole product.

Addition of di-*tert*-butyl sulfide to acetonitrile solutions containing the $[Ru^{IV}=O]^{2+}$ complex rapidly gives an initial intermediate having λ_{max} at 488 nm for the $[Ru\text{-}O \rightarrow S(tert\text{-}butyl)_2]^{2+}$ complex together with the peak at 442 nm for the $[Ru\text{-}NCCH_3]^{2+}$ complex as shown in the UV-vis spectral changes in Figure 1(c). The spectral patterns are quite similar to those previously observed in the epoxidation of olefins with an O-atom transfer mechanism.[11] As soon as it is formed, the O-bound sulfoxide complex undergoes solvolysis to give the $[Ru\text{-}NCCH_3]^{2+}$ complex and free sulfoxide in solutions. A sequence of reactions was also followed using ^1H NMR technique. Rapid formation of the O-bound com-

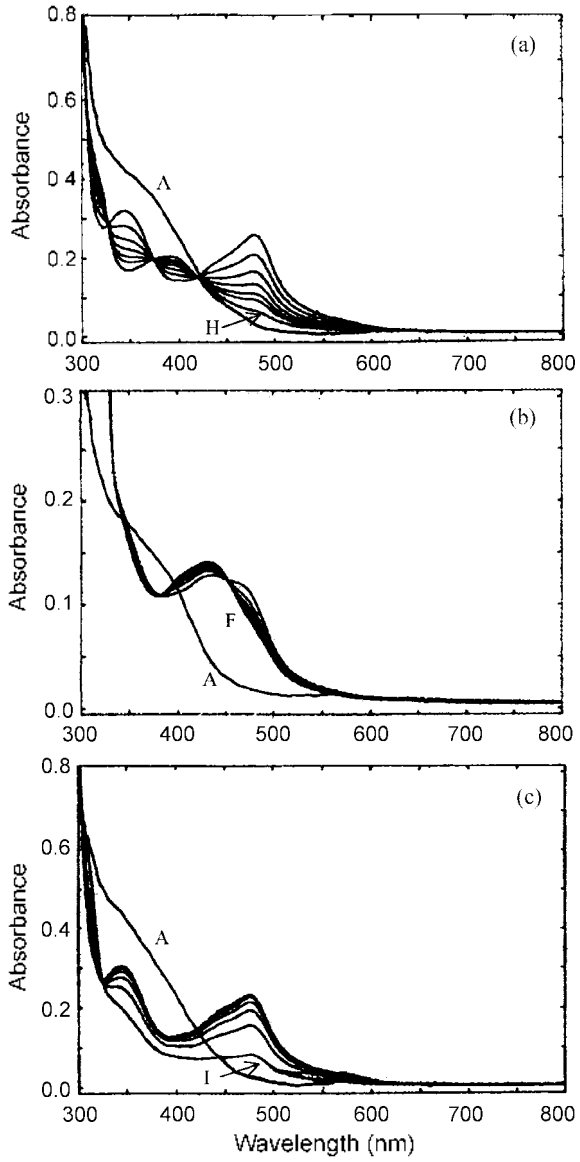

Figure 1. UV-vis spectral changes observed during the oxidation of (a) pentamethylene sulfide (1.93×10^{-2} M) by $[Ru(bpy)_2(py)(O)](ClO_4)_2$ (6.26×10^{-5} M) in CH_3CN: (A) 0, (B) 2, (C) 12, (D) 22, (E) 32, (F) 42, (G) 52, (H) 65 sec. (b) diphenyl sulfide (3.62×10^{-2} M) by $[Ru(bpy)_2(py)(O)](ClO_4)_2$ (4.14×10^{-5} M) in CH_3CN: (A) 0 (B) 20 sec, (C) 2.5, (D) 4, (E) 6, (F) 8, (G) 10 min. (c) di-*tert*-butyl sulfide (4.37×10^{-2} M) by $[Ru(bpy)_2(py)(O)](ClO_4)_2$ (7.17×10^{-5} M) in CH_3CN: (A) 0 (B) 1, (C) 3, (D) 5, (E) 7, (F) 9, (G) 11, (H) 13, (I) 15 min.

plex having a 6'-proton resonance at 9.49 ppm in addition to a lesser amount of solvolyzed complex at 9.42 ppm was observed in the part of ^1H NMR spectrum. After a long run, only solvolyzed product without any evidence of the formation of a S-bound sulfoxide complex was shown in the ^1H NMR spectrum of Figure 2(c).

The kinetics of the formation of an initial intermediate in the oxidation of organic sulfides by $[Ru^{IV}=O]^{2+}$ in CH_3CN were monitored at the wavelength around 480 nm. Over the limited concentration range studied, the reaction is first order in substrate and oxidant. Rate constant and kinetic data are

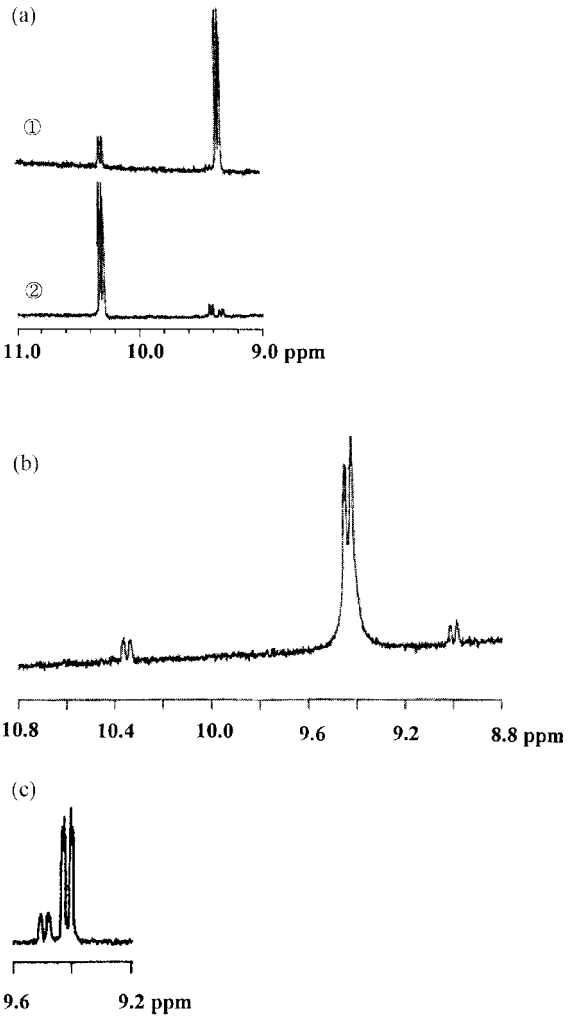

Figure 2. Partial ^1H NMR spectra of a reaction mixture in CD_3CN containing $[Ru(bpy)_2(py)(O)](ClO_4)_2$ (0.02 M) with (a) pentamethylene sulfide (0.03 M) after 15 min (①) and 6 hrs (②) (b) diphenyl sulfide (0.03 M) after 15 min (c) di-*tert*-butyl sulfide (0.04 M) after 50 min.

summarized in Table 1. The analysis of rate data shows that there is an evidence of significant steric effects in the rate of the formation of an O-bound intermediate for noncyclic sulfides. For cyclic organic sulfides, electronic effects prevail in the rate. Since no isomerization reaction takes place to lead to the S-bound sulfoxide complex, the rate is comparatively fast.

Table 1 shows activation parameters for the reactions of methyl sulfide with $[Ru^{IV}(bpy)_2(p\text{-}tert\text{-}butylpy)(O)]^{2+}$ in CH_3CN obtained from the plot of $\ln(k/T)$ *vs* $1/T$ over the temperature range of 15-40 °C and compares with those of $[Ru^{IV}(bpy)_2(py)(O)]^{2+}$. The rate enhancement for bis/bpy-py oxidant system must be attributed to the presence of less sterically hindered pyridine ligand compared to bis/bpy-*p*-*tert*-butylpy one. Though each potential of Ru(II/III) and Ru(III/IV) couples in two oxidants is quite similar, substitution of *p*-*tert*-butyl-py for py in bis/bpy-py system results in an increase in the oxidation potentials of approximately 0.06V. Considering the ability of the *p*-*tert*-butyl-py ligand

Table 1. Summary of Kinetic and Thermodynamic Parameters for the Oxidation Organic Sulfides by $[(bpy)_2(py)Ru(O)]^{2+}$ and $[(bpy)_2(p\text{-}tert\text{-}butylpy)Ru(O)]^{2+}$

Oxidant	Substrate	k, $M^{-1}s^{-1}$	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
$[(bpy)_2(py)Ru(O)]^{2+}$	methyl sulfide	17.1[a]	8.0(±0.9)[a]	-26(±3)[a]
$[(bpy)_2(py)Ru(O)]^{2+}$	ethyl sulfide	17.3		
$[(bpy)_2(py)Ru(O)]^{2+}$	*iso*-propyl sulfide	2.74		
$[(bpy)_2(py)Ru(O)]^{2+}$	*tert*-butyl sulfide	0.23		
$[(bpy)_2(py)Ru(O)]^{2+}$	phenyl sulfide	1.27		
$[(bpy)_2(py)Ru(O)]^{2+}$	propylene sulfide	4.77		
$[(bpy)_2(py)Ru(O)]^{2+}$	tetramethylene sulfide	15.5		
$[(bpy)_2(py)Ru(O)]^{2+}$	pentamethylene sulfide	21.1		
$[(bpy)_2(p\text{-}tert\text{-}butylpy)Ru(O)]^{2-}$	methyl sulfide	14.0	3.8(±0.5)	-40.0(±6)

[a]ref 5(b)

to provide stronger coordination ability to the ruthenium metal, it is explainable with a change in activation energy of oxygen atom transfer equal to ~4 kcal/mol. The results shown in Table 1 wouldn't suggest the apparent change in mechanism using different oxidant. The higher activation energy for sterically hindered bis/bpy-*p*-*tert*-butylpy system against bis/bpy-py one was observed. although the difference is not significant. Regarding the rate constant. a negative value for $\Delta S^{\ddagger}$ suggests associative mechanism. The difference of 14 eu in $\Delta S^{\ddagger}$ suggests the presence of more sterically hindered *p*-*tert*-butyl-py ligand compared to py one.

In summary it is clear that the oxidation of organic sulfides (SR_2) by $[Ru^{IV}=O]^{2-}$ in acetonitrile occurs by a net oxygen atom transfer. In an initial rapid step, the O-bound $[Ru^{II}\text{-}O \rightarrow SR_2]^{2+}$ intermediate is formed as an identifiable complex. Depending on the substrate using. an initial O-bound intermediate subsequently undergoes either far slower solvolysis reaction to give only solvolyzed $[Ru\text{-}NCCH_3]^{2-}$ product or fast isomerization reaction to afford both an isomerized S-bound $[Ru^{II}\text{-}S(\rightarrow O)R_2]^{2-}$ complex and a solvolyzed complex. The O-atom transfer reactivity suggests an electrophilic character at the oxo group. The oxidative reactivity toward dimethyl sulfide by two representative $[Ru^{IV}=O]^{2+}$ oxidants reported here will provide a more quantitative view of ruthenium mono-oxo oxidants.

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