

Oxidation of Hydrocarbons by Mono- and Dinuclear Ruthenium Quinone Complexes via Hydrogen Atom Abstraction

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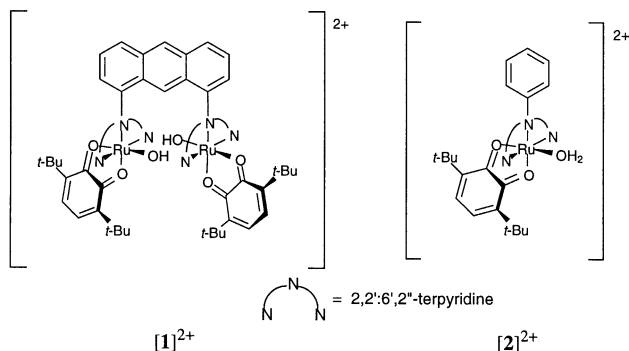
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Deprotonation and two-electron oxidation of $[\text{Ru}^{\text{II}}_2(\text{OH})_2(\text{Q})_2(\text{btpyan})]^{2+}$ ($\text{Q} = 3,6\text{-di}(\text{tert-butyl})\text{-1,2-quinone}$, $\text{btpyan} = 1,8\text{-bis}(2,2':6',2'')\text{-terpyridylanthracene}$) was converted to bis(ruthenium-oxo) complex $[\text{Ru}^{\text{IV}}_2(\text{O})_2(\text{Q})_2(\text{btpyan})]^{2+}$, which oxidized 1,3-cyclohexadiene and 1,2-dihydronaphthalene to corresponding aromatic compounds in the presence of AgClO_4 and $t\text{-BuOK}$. On the other hand, mononuclear complex $[\text{Ru}^{\text{II}}(\text{OH})_2(\text{Q})(\text{Ph-terpy})]^{2+}$ ($\text{Ph-terpy} = 4'\text{-phenyl-2,2':6',2''-terpyridine}$, $[\mathbf{2}]^{2+}$) was converted to $[\text{Ru}^{\text{IV}}(\text{OH})(\text{Q})(\text{Ph-terpy})]^{2+}$ under the similar conditions, but displayed the low activity for the oxidation compared with the dinuclear complex $[\mathbf{1}]^{2+}$.

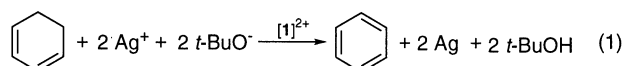
High valent transition metal-oxo complexes work as active species in biological and chemical oxidation of various organic substrates.^{1,2} Several ruthenium-oxo complexes have been reported as functional models for enzymatic reactions, and some of them have proven to hydroxylize and epoxidize hydrocarbons in the presence of dioxygen,³ peroxides such as H_2O_2 and $t\text{-BuOOH}$,⁴ and pyridine- N -oxides⁵ as oxygen sources. Oxo complexes are also generated by deprotonation of metal-aqua or metal-hydroxo complexes coupled with oxidation.⁶ We have reported that the dinuclear ruthenium-hydroxo complex $[\mathbf{1}]^{2+}$ with two $\text{Ru}(\text{Q})(\text{OH})$ units bridged by btpyan lig-



and reversibly dissociates protons and the oxidized form of resultant bis(ruthenium-oxo) complex worked as a good electrode catalyst of the water-oxidation to dioxygen.⁷ We describe here that the dinuclear oxo complex derived from $[\mathbf{1}]^{2+}$ has abilities of oxidation of not only water but also hydrocarbons by C-H bond cleavage in the presence of Ag^+ as a mild co-oxidant, along with the comparison of the activity of $[\mathbf{1}]^{2+}$ and the corresponding mononuclear complex $[\mathbf{2}]^{2+}$ toward the oxidation.

$t\text{-BuOK}$ (6.0 μmol) was added to the violet acetone solution of $[\mathbf{1}](\text{SbF}_6)_2$ (3.0 μmol), 1,3-cyclohexadiene (3.0 μmol)

and AgClO_4 (6.0 μmol) at room temperature in the air. The reaction was completed in one minute, and benzene was produced in a 90% yield with silver powder (Eq 1). After the reac-



tion, regeneration of $[\mathbf{1}]^{2+}$ was confirmed by the ESI-MS spectra of the reaction mixture. Benzene was produced again by the further addition of cyclohexadiene, AgClO_4 and $t\text{-BuOK}$ to the solution, though the yield of benzene decreased to an about 80% in the second reaction. Similarly, $[\mathbf{1}]^{2+}$ showed the high reactivity of the oxidation of 1,2-dihydronaphthalene to naphthalene under the same reaction conditions (Table 1).

Table 1 Oxidation reactions of hydrocarbons by di- and mononuclear ruthenium-quinone complexes ($[\mathbf{1}](\text{SbF}_6)_2$, $[\mathbf{2}](\text{SbF}_6)_2$) in the presence of AgClO_4 and $t\text{-BuOK}$

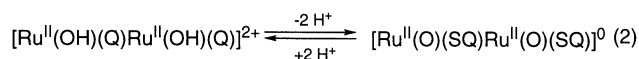
| Run | Substrates | Products | Yields /% | |
|-----|------------------------|-------------|-------------------------------|-------------------------------|
| | | | $[\mathbf{1}]^{2+ \text{ a}}$ | $[\mathbf{2}]^{2+ \text{ b}}$ |
| 1 | 1,3-cyclohexadiene | benzene | 90 | 14 |
| 2 | 1,2-dihydronaphthalene | naphthalene | 94 | 5 |
| 3 | 9,10-dihydroanthracene | anthracene | 0 | 42 |

^aAn acetone solution (0.5 ml) of $[\mathbf{1}](\text{SbF}_6)_2$ (3.0 μmol), substrate (3.0 μmol) and AgClO_4 (6.0 μmol) was stirred at room temperature in the air. A MeOH solution of $t\text{-BuOK}$ (6.0 μmol) was added to the acetone solution. The yields of products were determined by HPLC. ^bAn acetone solution (0.5 ml) of $[\mathbf{2}](\text{SbF}_6)_2$ (6.0 μmol), substrate (3.0 μmol) and AgClO_4 (6.0 μmol) was stirred at room temperature in the air. A MeOH solution of $t\text{-BuOK}$ (6.0 μmol) was added to the acetone solution. The yields of products were determined by HPLC.

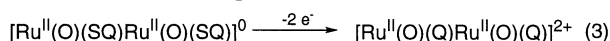
Dehydrogenation of 1,3-cyclohexadiene and 1,2-dihydronaphthalene also proceeded in the presence of the mononuclear complex $[\mathbf{2}]^{2+}$ under the similar reaction conditions, but the yields of benzene and naphthalene were quite low compared with those in the reactions catalyzed by $[\mathbf{1}]^{2+}$ (Runs 1 and 2). On the contrary, 9,10-dihydroanthracene was not oxidized by $[\mathbf{1}]^{2+}$ at all, and $[\mathbf{2}]^{2+}$ showed relatively high activity for the oxidation to give anthracene (42% yield, Run 3). The dehydrogenation reactions of the substrates in Table 1 did not proceed at all in case of the absence of either AgClO_4 , $t\text{-BuOK}$ or $[\mathbf{1}]^{2+}$ (or $[\mathbf{2}]^{2+}$). The active species of the oxidation reactions, therefore, is the oxidized form of $[\mathbf{1}]^{2+}$ or $[\mathbf{2}]^{2+}$ under basic conditions.

The violet MeOH solution of $[\mathbf{1}](\text{SbF}_6)_2$ showed the characteristic $\text{Ru}(\text{II})$ to quinone charge-transfer (MLCT) band at 576 nm. An addition of 2.0 equiv of $t\text{-BuOK}$ to the solution

resulted in the complete loss of the band 576 nm and an appearance of a new band at 850 nm assigned to Ru(II) to semiquinone charge-transfer (MLCT) band.^{8,9} Acidification of the solution by an addition of 2.0 equiv of HClO₄ to the solution completely restored the 576 nm band and disappeared the 850 nm band. Such the reversible change of the MLCT band of [1]²⁺ from 576 nm to 850 nm is explained by the reduction of quinone to semiquinone coupled with the deprotonation/protonation equilibrium of the hydroxo ligand of the dinuclear complex. Thus, deprotonation of [1]²⁺ produced [Ru^{II}(O)(SQ)Ru^{II}(O)(SQ)]⁰ (SQ = 3,6-di(*tert*-butyl)-1,2-semiquinone) (Eq 2). Cyclic



voltammetry of [Ru^{II}(O)(SQ)Ru^{II}(O)(SQ)]⁰ in MeOH revealed that the redox potentials of the [Ru^{II}(O)(SQ)Ru^{II}(O)(SQ)]⁰/[Ru^{II}(O)(Q)Ru^{II}(O)(SQ)]⁺ couple and the [Ru^{II}(O)(Q)Ru^{II}(O)(SQ)]⁺/[Ru^{II}(O)(Q)Ru^{II}(O)(Q)]²⁺ one were +0.30 V and +0.40 V (vs Ag/AgCl), respectively, and no other oxidation wave appeared up to 1.0 V in MeOH. Thus, [Ru^{II}(O)(Q)Ru^{II}(O)(Q)]²⁺ must be formed in the treatment of [1]²⁺ with Ag⁺ under basic conditions (Eq. 3).¹⁰



The mononuclear complex [2]²⁺ also displayed the Ru^{II} to quinone MLCT band at 576 nm in MeOH, which shifted to 869 nm due to formation of the [Ru^{II}(OH)(SQ)]⁺ moiety upon the treatment of the solution with *t*-BuOK. The p*K*_a value of the resultant [Ru^{II}(OH)(SQ)]⁺ was too large to form the oxo-complex in acetone.⁸ Based on the observation that [Ru^{II}(OH)(SQ)]⁺ was oxidized to [Ru^{II}(OH)(Q)]²⁺ at +0.07 V and the latter was not further oxidized in acetone, [2]²⁺ was converted to [Ru^{II}(OH)(Q)]²⁺ under the experimental conditions of Table 1.

The active species in the dehydrogenation reactions by [1]²⁺ and [2]²⁺ (Table 1) are [Ru^{II}(O)(Q)Ru^{II}(O)(Q)]²⁺ and [Ru^{II}(OH)(Q)]²⁺, respectively, which reasonably explain the regeneration of [1]²⁺ and [2]²⁺ after the reactions because of the abstraction of hydrogen atoms of the substrates.

The striking characteristic of the reactivity of [1]²⁺ is the high activity for cleavage of the vicinal two C–H bonds (Table 1, Runs 1 and 2) and no ability to abstract of hydrogen atoms of 9,10-dihydroanthracene (Run 3). On the other hand, [2]²⁺ showed the reverse reactivity: low activity for the abstraction of the vicinal hydrogen atoms and high ability to oxidize 9,10-dihydroanthracene. The difference in the reactivity of [1]²⁺ and [2]²⁺ for these substrates, therefore, is explained by the view that the dimeric [Ru^{II}(O)(Q)Ru^{II}(O)(Q)]²⁺ has an ability to cleave the vicinal two C–H bonds simultaneously with the regeneration of [1]²⁺, while the abstraction of H atom from these substrates by monomeric [Ru^{II}(OH)(Q)]²⁺ inevitably produces free radical species unless two molecules of [Ru^{II}(OH)(Q)]²⁺ participate in the cleavage of the vicinal two C–H bonds at the same time. The abstraction of the vicinal hydrogen atoms by [1]²⁺, therefore, is kinetically advantageous compared with that by [2]²⁺. Two hydroxo groups of [1]²⁺ must be located in the cavity of the dimeric linkage. Inability of [1]²⁺ for the oxidation of 9,10-dihydroanthracene apparently results from the steric hindrance for the approach to the oxo group in the cavity of dimeric linkage. On the other hand, two

molecules of [2]²⁺ would be able to participate in the abstraction of two hydrogen atoms of 9,10-dihydroanthracene (Run 3).

The active species in the present study were derived from [1]²⁺ and [2]²⁺ by taking advantage of the quinone/semiquinone redox reaction coupled with the acid–base equilibrium but not by the redox reactions of the central Ru(II)/Ru(III) redox couples. Especially, it is worthy to note from the viewpoint of biochemistry that [1]²⁺ showed activities for oxidation reactions of both water and hydrocarbons.

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