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

Tohru Wada, Kiyoshi Tsuge, and Koji Tanaka*
Department of Structural Molecular Science, Graduate University for Advanced Studies. 38 Nishigonaka, Myodaiji, Okazaki, Aichi 444-8585
Institute for Molecular Science. 38 Nishigonaka, Myodaiji, Okazaki, Aichi 444-8585

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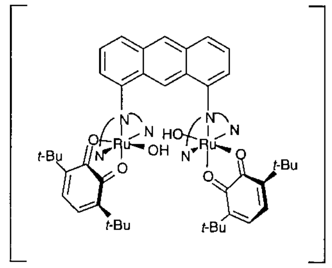
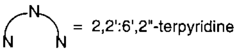
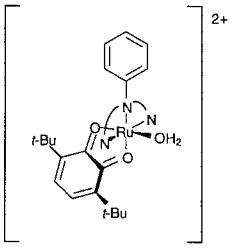
Deprotonation and two-electron oxidation of $[Ru^{II}_2(OH)_2(Q)_2(btpyan)]^{2+}$ (Q = 3,6-di(*tert*-butyl)-1,2-quinone, btpyan = 1,8-bis(2,2':6',2''-terpyridyl)anthracene) was converted to bis(ruthenium–oxo) complex $[Ru^{II}_2(O)_2(Q)_2(btpyan)]^{2+}$, which oxidized 1,3-cychrohexadiene and 1,2-dihydronaphtalene to corresponding aromatic compounds in the presence of $AgClO_4$ and *t*-BuOK. On the other hand, mononuclear complex $[Ru^{II}(OH_2)(Q)(Ph\text{-}terpy)]^{2+}$ (Ph-terpy = 4'-phenyl-2,2':6',2''-terpyridine, $[\mathbf{2}]^{2+}$) was converted to $[Ru^{II}(OH)(Q)(Ph\text{-}terpy)]^{2+}$ 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*-BuOOH,[4] and pyridine-*N*-oxides[5] 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 Ru(Q)(OH) units bridged by btpyan ligand 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.



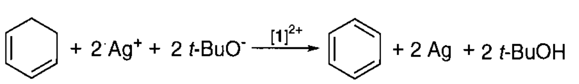
$[\mathbf{1}]^{2+}$





$[\mathbf{2}]^{2+}$

t-BuOK (6.0 µmol) was added to the violet acetone solution of $[\mathbf{1}](SbF_6)_2$ (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 reaction, 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*-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).



(1)

Table 1 Oxidation reactions of hydrocarbons by di- and mononuclear ruthenium-quinone complexes ($[\mathbf{1}](SbF_6)_2$, $[\mathbf{2}](SbF_6)_2$) in the presence of $AgClO_4$ and *t*-BuOK

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

[a] An acetone solution (0.5 ml) of $[\mathbf{1}](SbF_6)_2$ (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*-BuOK (6.0 µmol) was added to the acetone solution. The yields of products were determined by HPLC. [b] An acetone solution (0.5 ml) of $[\mathbf{2}](SbF_6)_2$ (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*-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*-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 $[\mathbf{1}](SbF_6)_2$ showed the characteristic Ru(II) to quinone charge-transfer (MLCT) band at 576 nm. An addition of 2.0 equiv of *t*-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 $HClO_4$ to the solution completely restored the 576 nm band and disappeared the 850 nm band. Such the reversible change of the MLCT band of $[\mathbf{1}]^{2+}$ 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 $[\mathbf{1}]^{2+}$ produced $[Ru^{II}(O)(SQ)Ru^{II}(O)(SQ)]^0$ (SQ = 3,6-di(*tert*-butyl)-1,2-semiquinone) (Eq 2). Cyclic

$$[Ru^{II}(OH)(Q)Ru^{II}(OH)(Q)]^{2+} \xrightleftharpoons[+2\,H^+]{-2\,H^+} [Ru^{II}(O)(SQ)Ru^{II}(O)(SQ)]^0 \quad (2)$$

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 $[\mathbf{1}]^{2+}$ with Ag^+ under basic conditions (Eq. 3).[10]

$$[Ru^{II}(O)(SQ)Ru^{II}(O)(SQ)]^0 \xrightarrow{-2\,e^-} [Ru^{II}(O)(Q)Ru^{II}(O)(Q)]^{2+} \quad (3)$$

The mononuclear complex $[\mathbf{2}]^{2+}$ 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 pK_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, $[\mathbf{2}]^{2+}$ was converted to $[Ru^{II}(OH)(Q)]^{2+}$ under the experimental conditions of Table 1.

The active species in the dehydrogenation reactions by $[\mathbf{1}]^{2+}$ and $[\mathbf{2}]^{2+}$ (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 $[\mathbf{1}]^{2+}$ and $[\mathbf{2}]^{2+}$ after the reactions because of the abstraction of hydrogen atoms of the substrates.

The striking characteristic of the reactivity of $[\mathbf{1}]^{2+}$ 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, $[\mathbf{2}]^{2+}$ 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 $[\mathbf{1}]^{2+}$ and $[\mathbf{2}]^{2+}$ 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 $[\mathbf{1}]^{2+}$, 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 $[\mathbf{1}]^{2+}$, therefore, is kinetically advantageous compared with that by $[\mathbf{2}]^{2+}$. Two hydroxo groups of $[\mathbf{1}]^{2+}$ must be located in the cavity of the dimeric linkage. Inability of $[\mathbf{1}]^{2+}$ 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 $[\mathbf{2}]^{2+}$ 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 $[\mathbf{1}]^{2+}$ and $[\mathbf{2}]^{2+}$ 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 $[\mathbf{1}]^{2+}$ showed activities for oxidation reactions of both water and hydrocarbons.

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10 Controlled-potential electrolysis at +0.55 V (vs Ag/AgCl) of a methanolic solution of $[Ru(O)(SQ)Ru(O)(SQ)]^0$ (λ_{max} = 850 nm) resulted in formation of $[Ru(O)(Q)Ru(O)(Q)]^{2+}$ (λ_{max} = 582 nm) .