

A Kinetic Study on the Reactivity of a *cis*-Dioxoruthenium(VI) Complex. Oxidation of Alcohols, Aromatic Hydrocarbons, and Alkenes by *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺

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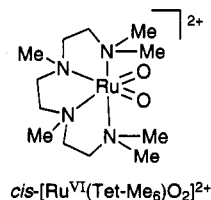
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The kinetics of oxidation of alcohols, aromatic hydrocarbons, and alkenes by *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺ (Tet-Me₆ = *N,N,N',N'*-tetramethyl-3,6-diazaoctane-1,8-diamine) have been studied. In general, the oxidation chemistry of *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺ is similar to those of *trans*-dioxoruthenium(VI) compounds such as *trans*-[Ru^{VI}(N₂O₂)O₂]²⁺ (N₂O₂ = 1,12-dimethyl-3,4:9,10-dibenzo-1,12-diaza-5,8-dioxacyclopentadecane) and *trans*-[Ru^{VI}(pytn)O₂]²⁺ (pytn = *N,N'*-dimethylbis(2-pyridylmethyl)-propylenediamine). The oxidation is first-order with respect to *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺ and organic substrates and is accompanied by large and negative ΔS^\ddagger . Large k_H/k_D values were found for the oxidation of alcohols. A linear Hammett plot for the oxidation of para-substituted benzyl alcohols with a slope of -1.0 was obtained. For alcohol oxidation, a charge-transfer mechanism involving hydride abstraction has been proposed. Oxidation of toluene, ethylbenzene, and cumene by *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺ gave benzaldehyde, acetophenone/*sec*-phenylisopropyl alcohol, and 2-phenylisopropyl alcohol, respectively. A k_H/k_D value of 11 has been found for the oxidation of ethylbenzene. In the oxidation of these aromatic hydrocarbons, the key step likely involves C–H bond activation in the transition state. Allylic oxidation is the major reaction pathway in the cyclohexene oxidation. In the oxidation of alkenes, both C=C bond cleavage product(s) and epoxides were found. The Hammett plot for the oxidation of para-substituted styrenes is linear with a slope of -2.0 . The oxidation likely proceeds through a charge-transfer mechanism.

Introduction

High-valent oxo and dioxo complexes of ruthenium in the oxidation state of IV, V, and VI have been receiving current interest because of their applications in organic oxidation.^{1–3} Previously, we have isolated a number of d² *trans*-dioxoruthenium(VI) complexes containing π -aromatic diimines⁴ and macrocyclic tertiary amines ligands⁵ and have demonstrated that some of their physical properties, such as redox potentials, as well as reactivities, can be tuned by suitable ligand modification. Reports on d² *cis*-dioxo complexes are sparse,^{6–9} and not all the structurally characterized *cis*-dioxo complexes are

reactive toward organic oxidation. Furthermore, some reactive dioxo complexes like *cis*-[Ru^{VI}(bpy)₂O₂]²⁺ (bpy = 2,2'-bipyridine) are unstable with respect to *trans*-dioxo formation.⁸ We and Drago and co-workers have reported that, with the use of sterically hindered diimines like 6,6-dichloro-2,2'-bipyridine (6,6'-Cl₂bpy)^{7b} and 2,9-dimethyl-1,10-phenanthroline (2,9-Me₂phen),⁶ isomerization of *cis*-[Ru^{VI}(L)₂(OH₂)₂]²⁺ (L = 6,6'-Cl₂bpy, 2,9-Me₂phen) to the *trans*-isomer is prevented and stable *cis*-[Ru^{VI}(L)₂O₂]²⁺ has been successfully isolated. In 1992, the synthesis and X-ray structure of a *cis*-dioxoruthenium(VI) complex, *cis*-[Ru^{VI}(Tet-Me₆)O₂](ClO₄)₂, bearing an open-chain N₄ donor ligand, Tet-Me₆ = *N,N,N',N'*-tetramethyl-3,6-dimethyl-3,6-diazaoctane-1,8-diamine, was reported.⁹ Contrary to the extreme reactivities of the *cis*-dioxoruthenium(VI)-containing π -aromatic diimines, *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺ (ClO₄)₂ is relatively stable in solution.



In the d² Ru(VI) system, *trans*-dioxoruthenium(VI) is stabilized compared with *cis*-dioxoruthenium(VI) because of the d_π (Ru) and p_π (O²⁻) interaction.¹⁰ It is interesting to compare *trans*-[Ru^{VI}(14-TMC)O₂]²⁺¹¹ (14-TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclopentadecane) and *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺⁹ because both complexes contain chelating tetradentate tertiary amine ligand. The much

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longer Ru=O bond distance [1.71 vs 1.795 Å]^{11a} and the higher E° value [0.67 vs 0.80 V at pH = 1]^{11b} for the latter complex suggest that, with the same ligand environment, *cis*-dioxoruthenium(VI) should be a better oxidant. A preliminary study showed that *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺ could oxidize a variety of organic substrates whereas *trans*-[Ru^{VI}(14-TMC)O₂]²⁺ is unreactive toward oxidation of alkenes and aromatic hydrocarbons under the same conditions. Herein is described a kinetic study on the oxidation of alcohols, aromatic hydrocarbons, and alkenes by *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺.

Experimental Section

Materials. Acetonitrile (Mallinkrodt AR) used in kinetic studies was first treated with KMnO₄ overnight and then distilled over CaH₂ under a nitrogen atmosphere. Organic substrates were purified by distillation and/or recrystallization, and the purity was checked by gas chromatography and ¹H NMR spectroscopy. *cis*-[Ru^{VI}(Tet-Me₆)O₂](ClO₄)₂ was prepared as described previously.⁹

Instrumentation and Technique. The details of the instrumentations for the characterization of the metal complex and organic products after oxidation have been reported in previous works.⁹

Kinetic studies on the oxidation of organic substrates by *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺ were performed with a Unicam SP8000 spectrophotometer which was linked to an Apple II microcomputer via AD/DA interface card (ADA laboratory, Interactive Microware, Inc.). The reactions were followed by monitoring the decrease in absorbance of *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺ at 325 nm under the condition that the concentration of organic substrate was at least a 100-fold excess of the ruthenium oxidant. Pseudo-first-order rate constants, k_{obs} , were obtained by nonlinear least-square fits of A_t to time t according to the equation

$$A_t = A_\infty + (A_0 - A_\infty) \exp(-k_{\text{obs}}t)$$

where A_0 and A_∞ are the initial and final absorbances, respectively. Kinetic data over 3 half-lives were used for the fitting. Second-order rate constants k_2 were obtained from linear least-square fits of k_{obs} to [organic substrate]. Activation parameters ΔH^\ddagger and ΔS^\ddagger were obtained from the slope and intercept of plots of $\ln(k_2/T)$ vs $1/T$.

Results and Discussion

Oxidation of Alcohols. In general, alcohols (ROH) are oxidized by *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺ to the corresponding aldehydes and ketones in quantitative yields.⁹ In acetonitrile solution, and after prolonged reaction, *cis*-[Ru^{IV}(Tet-Me₆)(MeCN)₂](ClO₄)₂ could be isolated as the final ruthenium product, the structure of which has been characterized by X-ray crystal analysis.⁹ The reaction proceeds according to a stoichiometry, *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺:alcohol, of 1:1.⁹ As shown in Figure 1, spectral changes of the reaction show clean isosbestic points. The UV-vis spectrum of the ruthenium product of immediate reduction is in fact virtually identical to that of *cis*-[Ru^{IV}(Tet-Me₆)O(H₂O)]²⁺,¹² which was generated by constant potential electrolysis of *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺ in 0.1 M CF₃CO₂H. We tentatively assign it to be *cis*-[Ru^{IV}(Tet-Me₆)O(H₂O)]²⁺, although the alternate formulation [Ru^{IV}(Tet-Me₆)O(MeCN)]²⁺ cannot be excluded. Thus, alcohol

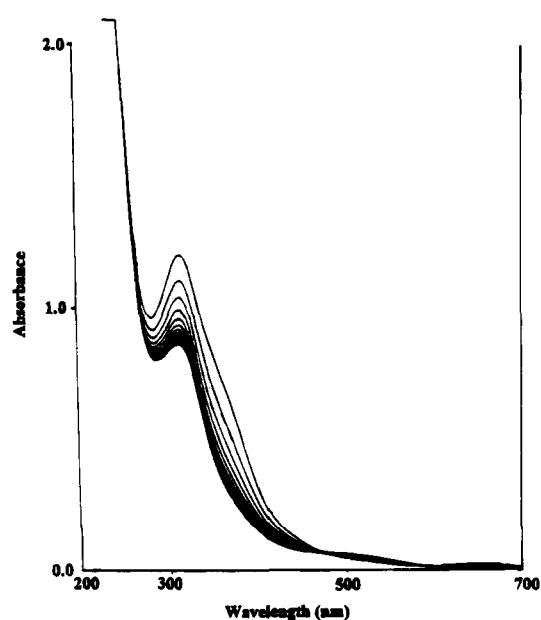


Figure 1. UV-vis spectral changes for the reaction between *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺ (10^{-3} M) and benzyl alcohol (0.1 M). Scan interval, 2 min.

Table 1. Second-Order Rate Constants for the Oxidation of Various Alcohols by *cis*-[Ru^{VI}(tet-Me₆)O₂]²⁺ in Acetonitrile at 298 K

alcohol	$k_2/\text{M}^{-1} \text{s}^{-1}$	potential ^a (V vs Ag/Ag ⁺)
methanol	$(1.23 \pm 0.05) \times 10^{-4}$	
methanol- <i>d</i> ₄	$(1.58 \pm 0.06) \times 10^{-5}$	
ethanol	$(6.17 \pm 0.29) \times 10^{-4}$	-2.61
propan-1-ol	$(1.09 \pm 0.04) \times 10^{-3}$	-2.56
cyclobutanol	$(1.39 \pm 0.06) \times 10^{-3}$	
propan-2-ol (H ₂ O)	$(2.40 \pm 0.07) \times 10^{-3}$	
propan-2-ol (D ₂ O)	$(2.36 \pm 0.07) \times 10^{-3}$	
propan-2-ol	$(1.84 \pm 0.07) \times 10^{-3}$	-2.50
propan-2-ol- <i>d</i> ₈	$(1.80 \pm 0.06) \times 10^{-4}$	
pentan-1-ol	$(1.96 \pm 0.07) \times 10^{-3}$	-2.46
benzyl alcohol (H ₂ O)	$(1.84 \pm 0.05) \times 10^{-2}$	
benzyl alcohol	$(1.60 \pm 0.05) \times 10^{-2}$	
benzylalcohol- α,α - <i>d</i> ₂	$(7.62 \pm 0.22) \times 10^{-4}$	
4-methoxybenzyl alcohol	$(3.19 \pm 0.12) \times 10^{-2}$	
4-methylbenzyl alcohol	$(2.39 \pm 0.08) \times 10^{-2}$	-1.59
4-chlorobenzyl alcohol	$(9.00 \pm 0.30) \times 10^{-3}$	-1.76
4-(trifluoromethyl)benzyl alcohol	$(3.10 \pm 0.09) \times 10^{-3}$	

^a Bard, A. J.; Lund, H. *Encyclopedia of Electrochemistry of the Elements, Organic Section*; Marcel Dekker, Inc.: New York, 1978.

oxidation by *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺ is a two-electron process involving reduction of Ru(VI) to Ru(IV).

Under the condition that [alcohol] \gg [Ru(VI)], a pseudo-first-order rate law

$$\text{rate} = k_{\text{obs}}[\text{Ru(VI)}]$$

can be established where $k_{\text{obs}} = k_2[\text{alcohol}]$. The values of the second-order rate constants at 25 °C are tabulated in Table 1. Large C-H deuterium isotope effects are observed for propan-2-ol, $k_{\text{H}}/k_{\text{D}} = 10$, for benzyl alcohol, $k_{\text{H}}/k_{\text{D}} = 21$, and for methanol, $k_{\text{H}}/k_{\text{D}} = 8$. Kinetic data for the calculation of activation parameters for the oxidation of benzyl alcohol, propan-2-ol, and cyclobutanol are summarized in Table 2. The entropy of activation, ΔS^\ddagger , is large and negative in all cases. The enthalpy of activation, ΔH^\ddagger , is slightly lower for the more reactive benzyl alcohol. The kinetic isotope effects and ΔS^\ddagger values

(12) *cis*-[Ru^{IV}(Tet-Me₆)O(H₂O)]²⁺ was generated by constant potential reduction of *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺ at 0.7 V vs SCE at pH = 1. *cis*-[Ru^{IV}(Tet-Me₆)O(H₂O)]²⁺ UV-vis (0.1 M CF₃CO₂H) [$\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{max}}/\text{mol}^{-1} \text{L cm}^{-1}$): 510 (70), 320 (850)]. Li, C. K. Ph.D. Thesis, The University of Hong Kong, 1991.

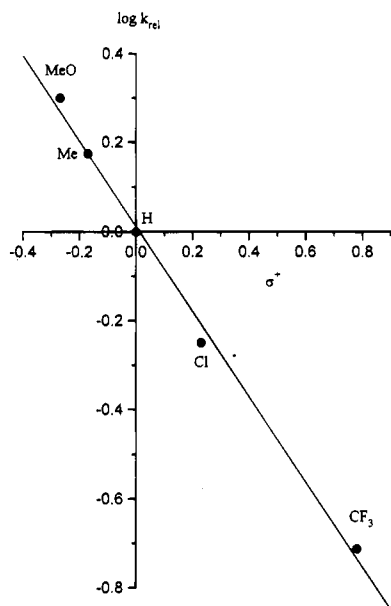
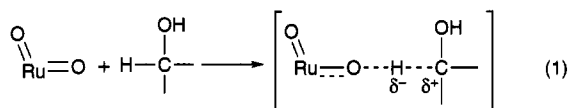


Figure 2. Hammett plot for the oxidation of *para*-substituted benzyl alcohols by *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺ in acetonitrile.

Table 2. Kinetic Data for the Oxidation of Benzyl Alcohol, Propan-2-ol, and Cyclobutanol by *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺ at Different Temperatures in Acetonitrile

substrate	temp/K	$k_2 \times 10^3 / \text{M}^{-1} \text{s}^{-1}$	$\Delta H^\ddagger / \text{kcal/mol}$	$\Delta S^\ddagger / \text{eu}$
benzyl alcohol	288	9.00 ± 0.31	12 ± 1	-24 ± 3
	298	16.0 ± 0.5		
	306	30.0 ± 1.2		
	313	58.0 ± 1.9		
propan-2-ol	288	1.02 ± 0.04	13 ± 1	-26 ± 4
	298	1.84 ± 0.07		
	306	3.55 ± 0.13		
	313	7.53 ± 0.30		
cyclobutanol	288	0.60 ± 0.02	14 ± 1	-22 ± 3
	298	1.39 ± 0.06		
	306	2.72 ± 0.011		
	313	5.16 ± 0.19		

imply association of the reactants and substantial C–H bond cleavage in the transition state. Equation 1 is tentatively suggested

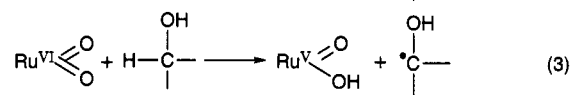
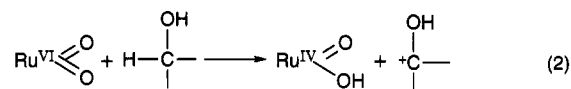


The Hammett plot for the oxidation of *para*-substituted benzyl alcohols in acetonitrile is shown in Figure 2. A linear plot with a slope of -1.0 is obtained, suggesting the substantial development of positive charge at the α -carbon atom of benzyl alcohol in the transition state. The ρ^+ value found in this work is comparable to the value of -1.2 obtained in the oxidation of *para*-substituted benzyl alcohols by *trans*-[Ru^{VI}(N₂O₂)(O₂)₂]²⁺ (N₂O₂ = 1,12-dimethyl-3,4:9,10-dibenzo-1,12-diaza-5,8-dioxacyclopentadecane). With reference to the data listed in Table 1, a linear free-energy relationship could also be established between the $\log(k_2)$ and the ionization potentials of alcohols demonstrating an important contribution of charge-transfer from the $\alpha(\text{C}-\text{H})$ bond to Ru=O.

Previous results on alcohol oxidation by a series of reactive *trans*-dioxoruthenium(VI) complexes showed a

linear free-energy relationship between $\log(k_2)$ and $E^\circ(\text{Ru}^{\text{VI/IV}})$.¹³ Slopes of -14.7 and -16.9 V^{-1} for propan-2-ol and benzyl alcohol, respectively, were obtained, and these values are close to the theoretical value of -16.8 V^{-1} predicted by the Marcus equation for a two-electron hydride-transfer reaction. By fitting the rate constants obtained in this work for oxidation of propan-2-ol and benzyl alcohol (k_2 for propan-2-ol and benzyl alcohol are 2.40×10^{-3} and $1.84 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$, respectively, and Ru(VI/IV) is 0.8 V at pH = 1.0) into the plots, we found that, within experimental errors, the data lie satisfactorily on straight lines as shown in Figure 3. It seems that oxidation of alcohols by *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺ and by *trans*-dioxoruthenium(VI) complexes are alike and both likely proceed via a common mechanism.

On the basis of the large and negative ΔS^\ddagger values, large kinetic isotope effects, and a linear free-energy relationship between $\log k_2$ and $E^\circ(\text{Ru}^{\text{VI/IV}})$, we propose that oxidation of alcohol by *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺ proceeds via eq 1. In this formulation, the $\alpha(\text{C}-\text{H})$ bond serves as the donor whereas the electrophilic Ru^{VI}=O moiety behaves as an acceptor. Previous works showed that oxidation of alcohols by RuO₄¹⁴ and [Ru^{IV}(bpy)₂(py)O]²⁺¹⁵ proceed by similar prior association of alcohol to the oxidant. The cleavage of the $\alpha(\text{C}-\text{H})$ bond to carbonyl compound could occur via a two-electron/one-proton transfer (hydride abstraction). However, a discrete hydride abstraction involving the formation of carbocation intermediate (eq 2) is unlikely, given the difference in



rates of oxidation of methanol and benzyl alcohol is only about 100 times. A concerted oxygen atom insertion into the $\alpha(\text{C}-\text{H})$ bond of alcohol could explain the small difference in rate constants listed in Table 1, but this suggestion contrasts with the large kinetic isotope effects found in this work. Unless other factor(s), such as nuclear tunneling, are important in determining the $k_{\text{H}}/k_{\text{D}}$ value,¹⁵ we prefer the head-on interaction between the $\alpha(\text{C}-\text{H})$ bond and Ru=O be involved in rate-determining step (eq 1). A mechanism involving two sequential one-electron transfers (eq 3) is unlikely because, for oxidation of cyclobutanol, this will lead to the generation of cyclobutoxy radical which is unstable with respect to the ring opening reaction.¹⁶ As reported in previous work, only cyclobutanone was formed exclusively.⁹

The kinetic data for the oxidation of propan-2-ol by some oxoruthenium complexes like RuO₄,¹⁶ RuO₄⁻,¹⁷ RuO₂²⁻¹⁷ are listed in Table 3. The data for *trans*-[Ru^{VI}(N₂O₂)O₂]²⁺¹³ are listed for comparison. Except for RuO₄⁻, they were all found to have similar ΔS^\ddagger (-20.3 to -28 eu) and ΔH^\ddagger (12.2 – 14 kcal mol^{-1}). The difference in reactivity for RuO₄⁻ could be inferred from the formation of acyclic products from the oxidation of

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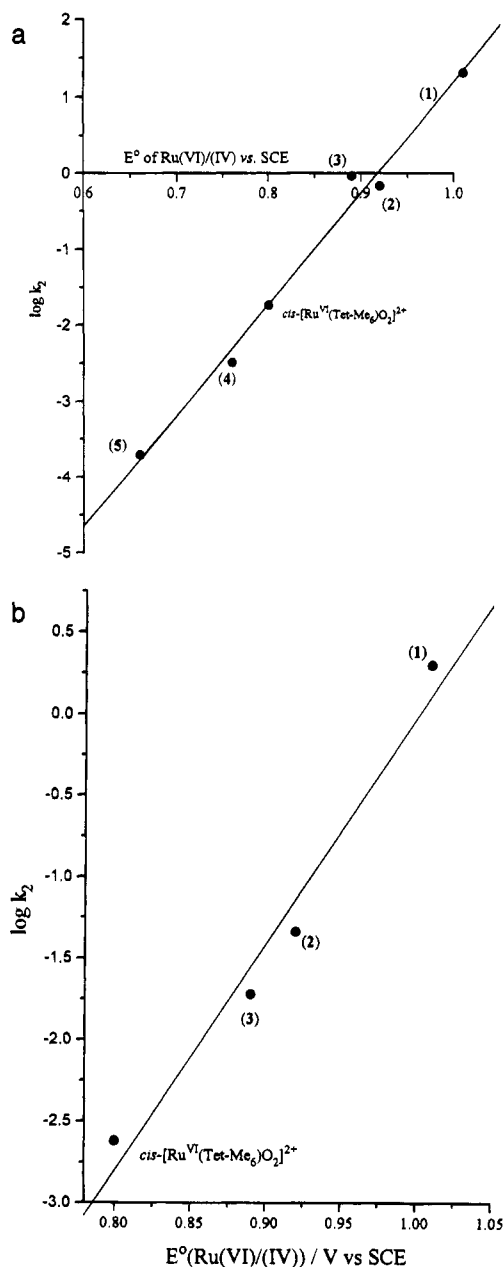


Figure 3. (a) Plot of $\log k_2$ vs E° of Ru(VI)/(IV) for the oxidation of benzyl alcohol by a series of dioxoruthenium complexes in H_2O : (1) *trans*- $[\text{Ru}^{\text{VI}}(\text{bpy})_2\text{O}_2]^{2+}$, (2) *trans*- $[\text{Ru}^{\text{VI}}(\text{N}_2\text{O}_2)\text{O}_2]^{2+}$, (3) *trans*- $[\text{Ru}^{\text{VI}}(\text{pytn})\text{O}_2]^{2+}$, (4) *trans*- $[\text{Ru}^{\text{VI}}(\text{CRMe}_3)\text{O}_2]^{2+}$ (CRMe₃ = meso-2,3,7,11-pentamethyl-3,7,11,17-tetraazabicyclo[11,3,1]-heptadeca-1(17),13,15-triene), (5) *trans*- $[\text{Ru}^{\text{VI}}(14\text{-TMC})\text{O}_2]^{2+}$. (b) Plot of $\log k_2$ vs E° of Ru(VI)/(IV) for the oxidation of 2-propanol by a series of dioxoruthenium complexes in H_2O : (1) *trans*- $[\text{Ru}^{\text{VI}}(\text{bpy})_2\text{O}_2]^{2+}$, (2) *trans*- $[\text{Ru}^{\text{VI}}(\text{N}_2\text{O}_2)\text{O}_2]^{2+}$, (3) *trans*- $[\text{Ru}^{\text{VI}}(\text{pytn})\text{O}_2]^{2+}$.

Table 3. Activation Parameters for the Oxidation of Propan-2-ol by Various High-Valent Oxoruthenium Complexes

oxidant	$\Delta H^\ddagger/\text{kcal/mol}$	$\Delta S^\ddagger/\text{eu}$
RuO_4^-	2.0 ± 0.2	-40 ± 1
RuO_4^{2-}	12.2 ± 0.2	-23 ± 1
<i>trans</i> - $[\text{Ru}^{\text{VI}}(\text{N}_2\text{O}_2)\text{O}_2]^{2+}$	12 ± 1	-28 ± 3
<i>cis</i> - $[\text{Ru}^{\text{VI}}(\text{tet-Me}_6)\text{O}_2]^{2+}$	13 ± 1	-26 ± 4

cyclobutanol. The low reactivity of HRuO_4^- that formed from an initial one-electron H-atom abstraction by RuO_4^- was proposed to be responsible for the diffusion of the free radical out of the cage, which then undergoes

Scheme 1

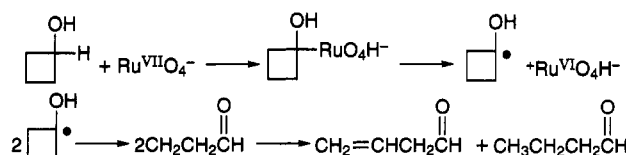


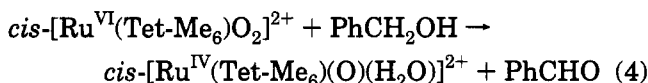
Table 4. Kinetic Data for the Oxidation of Aromatic Hydrocarbons by *cis*- $[\text{Ru}^{\text{VI}}(\text{tet-Me}_6)\text{O}_2]^{2+}$ in Acetonitrile at 298 K

substrate	$k_2/\text{M}^{-1} \text{s}^{-1}$	k_H/k_D
cumene	$(1.5 \pm 0.1) \times 10^{-3}$	
cumene (+0.05 M <i>t</i> -BuOH)	$(1.4 \pm 0.1) \times 10^{-3}$	
ethylbenzene	$(7.5 \pm 0.3) \times 10^{-4}$	
ethylbenzene- <i>d</i> ₁₀	$(6.8 \pm 0.3) \times 10^{-5}$	11
toluene	$(8.8 \pm 0.4) \times 10^{-5}$	

α -scission with the consequent formation of acyclic products. Thus, the mechanism can be divided for convenience into an initial formation of a loosely bound association complex followed by a redox step (Scheme 1).¹⁶

Oxidation of Aromatic Hydrocarbons. *cis*- $[\text{Ru}^{\text{VI}}(\text{Tet-Me}_6)\text{O}_2]^{2+}$ can oxidize toluene to benzaldehyde in acetonitrile at room temperature. With ethylbenzene, the secondary C-H bond is selectively oxidized to give acetophenone and *sec*-phenylethyl alcohol.⁹ It also selectively oxidizes tertiary C-H bonds of cumene to give 2-phenylisopropyl alcohol with a stoichiometry of (oxidant:cumene) 1:1.⁹ Repeating the stoichiometric reactions in an argon atmosphere gave similar results.

Similar to Figure 1, the UV-vis spectral changes of oxidation show similar isosbestic points (475 and 585 nm) indicating the reaction involves reduction of Ru(VI) to Ru(IV), and the UV-vis spectrum of the immediate ruthenium product is similar to that of *cis*- $[\text{Ru}^{\text{IV}}(\text{Tet-Me}_6)\text{O}(\text{OH}_2)]^{2+}$. The ruthenium product could be either *cis*- $[\text{Ru}^{\text{IV}}(\text{Tet-Me}_6)\text{O}(\text{OH}_2)]^{2+}$ or *cis*- $[\text{Ru}^{\text{IV}}(\text{Tet-Me}_6)\text{O}(\text{MeCN})]^{2+}$. The production of benzaldehyde and acetophenone in the stoichiometric oxidation of toluene and ethylbenzene could be accounted for by further oxidation of the intermediate alcohol by another molecule of *cis*- $[\text{Ru}^{\text{VI}}(\text{Tet-Me}_6)\text{O}_2]^{2+}$ as shown in eq 4.



The rate constant for the oxidation of benzyl alcohol is $1.6 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ (Table 1), which is 200 times faster than that of $8.8 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ for the oxidation of toluene. In order to avoid the secondary reduction of Ru(IV) by benzyl alcohol, a large excess (1000 times) of aromatic hydrocarbon was used in the kinetic studies. Under such conditions, the experimental rate law was found to be

$$\text{rate} = k_{\text{obs}}[\text{Ru}(\text{VI})] \quad (5)$$

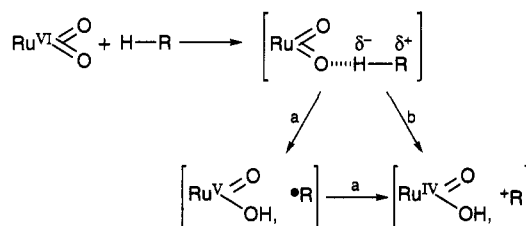
where

$$k_{\text{obs}} = k_2[\text{aromatic hydrocarbon}]$$

The second order rate constants are summarized in Table 4. The rate constants have been found to follow the order toluene \ll ethylbenzene $<$ cumene. Despite a large difference in the α (C-H) bond strength of cumene and ethylbenzene, their second-order rate constants disproportionately show only a small difference. A

Table 5. Kinetic Data for the Oxidation of Cumene and Ethylbenzene by *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺ at Different Temperatures in Acetonitrile

substrate	temp/K	$k_2 \times 10^3$	$\Delta H^\ddagger/\text{kcal/mol}$	$\Delta S^\ddagger/\text{eu}$
cumene	298	1.5 ± 0.1	14 ± 1	-25 ± 3
	306	2.9 ± 0.2		
	313	5.2 ± 0.2		
	320	8.1 ± 0.3		
ethylbenzene	298	0.75 ± 0.03	13 ± 1	-30 ± 4
	306	1.3 ± 0.1		
	313	2.2 ± 0.1		
	320	3.5 ± 0.2		

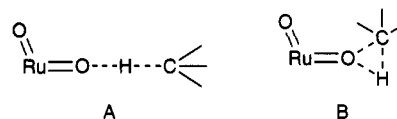
Scheme 2

similar finding has been reported for the *trans*-dioxoruthenium(VI) system.¹⁸ On the other hand, the increase in alkyl substituents at the α -carbon (e.g., cumene) can disperse the positive charge built up at the α -carbon atom during the redox step and hence speed up the reaction rate.

Large deuterium isotope effects have been used to adduce a process that involves considerable C–H bond cleavage in the transition state. A k_H/k_D of 11 has been obtained for the oxidation of ethylbenzene, and it is similar to k_H/k_D values of 12 and 16 found in *trans*-[Ru^{VI}(N₂O₂)O₂]²⁺¹⁸ and *trans*-[Ru^{VI}(pytn)O₂]²⁺¹⁸ (pytn = *N,N'*-dimethylbis(2-pyridylmethyl)propylenediamine), respectively. Activation parameters for the oxidation of cumene and ethylbenzene were determined over the temperature range 291–313 K (Table 5). Both reactions are accompanied by similar ΔS^\ddagger and ΔH^\ddagger values. The negative ΔS^\ddagger values and large kinetic isotopic effect on the rate constants indicate a substantial interaction between the Ru=O moiety and the C–H bond of the aromatic hydrocarbon in transition state.

Either a hydrogen atom, a hydride abstraction mechanism, or a concerted oxygen atom insertion into the C–H bond is possible. Outersphere electron transfer from the C–H bond to the Ru=O oxidant is unlikely based on thermodynamic standpoint. The $E_{1/2}(\text{Ru(VI)}/\text{Ru(V)})$ of *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺ (0.53 V vs Ag/AgNO₃) is far too low compared to the one-electron oxidation potentials of all aromatic hydrocarbons used in this work for outersphere electron transfer to be a viable pathway. Similarly, there is no evidence for the formation of product(s) arising from the coupling of the PhC(CH₃)₂ radicals in case of cumene oxidation. Furthermore, the yields of the organic products and the rate constants of the oxidation are independent of the addition of radical scavengers. These findings strongly argue against a mechanism involving the formation of out-cage radical intermediate(s). The proposed key step of C–H bond activation is outlined in Scheme 2.

Pathway a involves an initial hydrogen atom abstraction followed by a rapid in-caged one-electron transfer before the radical intermediate R• and O=Ru^VOH diffuse

Chart 1**Table 6. Second-Order Rate Constants for the Oxidation of Alkenes by *cis*-[Ru^{VI}(tet-Me₆)O₂]²⁺ in Acetonitrile at 298 K**

alkene	$k_2 \times 10^3/\text{M}^{-1} \text{s}^{-1}$
4-methoxystyrene	110 ± 4
4-methylstyrene	14.0 ± 0.5
cyclohexene	13.0 ± 0.5
norbornene	9.87 ± 0.32
cyclooctene	7.26 ± 0.18
4-fluorostyrene	4.04 ± 0.14
α -methylstyrene	3.97 ± 0.14
styrene	3.09 ± 0.09
4-chlorostyrene	2.04 ± 0.07
<i>trans</i> - β -methylstyrene	1.13 ± 0.05
<i>cis</i> -stilbene	0.49 ± 0.02

out to the solution. Such a pathway would be very difficult to distinguish from a two-electron hydride abstraction mechanism (b). A concerted oxygen atom insertion into a C–H bond is also likely, given the small difference in the rate constants and in ΔS^\ddagger values for the oxidation of cumene and ethylbenzene. However, the large k_H/k_D value for ethylbenzene oxidation could not be rationalized. May be the structure of the transition state is in between that of **A** and **B** (Chart 1), and other factor(s), such as the tunnelling effect, are responsible for the large k_H/k_D value.

Oxidation of Alkenes. Oxidation of alkenes by *cis*-[Ru^{VI}(Tet-Me₆)O₂](ClO₄)₂ gave both epoxides and C=C cleavage products, and the spectral changes of oxidation show clean isosbestic points. As in the oxidation of alcohols and aromatic hydrocarbons, the immediate reaction product could be either *cis*-[Ru^{IV}(Tet-Me₆)(O)(H₂O)]²⁺ or *cis*-[Ru^{IV}(Tet-Me₆)(O)(CH₃CN)]²⁺, both of which may have very similar UV–vis absorption spectra. The yields of organic products were unaffected when the reaction took place in an inert atmosphere. Oxidation of styrene gave predominantly benzaldehyde together with a small amount of styrene oxide,⁹ and the UV–vis spectral changes are similar to those shown in Figure 1. For [alkene] \gg [Ru(VI)] (at least 100 times), the experimental rate law, rate = $k_{\text{obs}}[\text{Ru(VI)}]$ ($k_{\text{obs}} = k_2[\text{alkene}]$) was found. The kinetic results of alkene oxidation by *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺ at 298 K in acetonitrile are listed in Table 6. No rate saturation was ever observed. The temperature dependence of k_2 for oxidation of styrene, norbornene, and cyclohexene has been investigated, and their activation parameters are tabulated in Table 7. The ΔS^\ddagger values found in this work are comparable to those for oxidation by *trans*-[Ru^{VI}(N₂O₂)(O)₂]²⁺. ($\Delta S^\ddagger = -22$ eu for styrene, -25 eu for norbornene, and -23 eu for cyclohexene.)¹⁹

The electronic effects on the rate of styrene oxidation were studied systematically by replacing *para*-substituents. Figure 4 shows the Hammett plot for the oxidation of *para*-substituted styrenes by *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺. A linear plot with a ρ^+ value of -2.0 was obtained.

Regarding the mechanism, a concerted oxygen atom insertion seems improbable because of the nonstereorententive nature of the oxidation. In previous work, *cis*-

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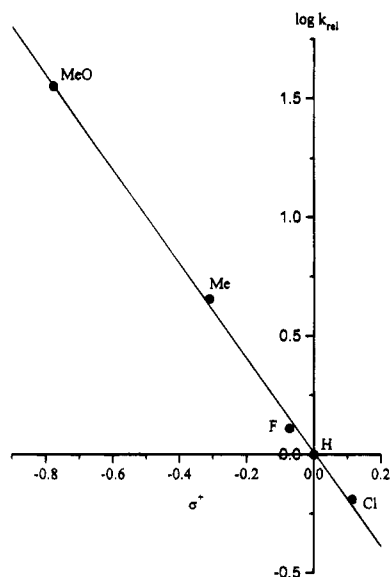


Figure 4. Hammett plot for the oxidation of *para*-substituted styrenes by *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺ in acetonitrile at 298 K.

Table 7. Representative Kinetic Data for the Oxidation of Cyclohexene, Styrene, and Norbornene by [Ru^{VI}(tet-Me₆)O₂]²⁺ in Acetonitrile at 298 K

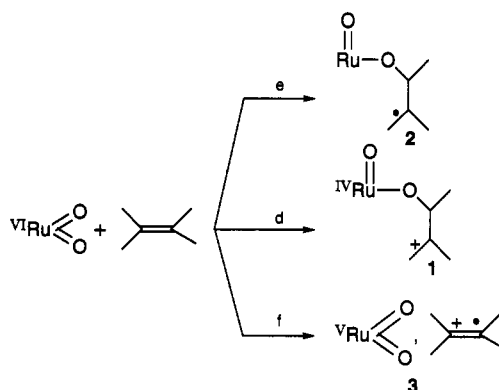
substrate	temp/K	$k_2 \times 10^3 / \text{M}^{-1} \text{s}^{-1}$	$\Delta H^\ddagger / \text{kcal/mol}$	$\Delta S^\ddagger / \text{eu}$
cyclohexene	288	6.2 ± 0.8	13 ± 1	-24 ± 2
	298	13.0 ± 0.5		
	306	24.0 ± 0.9		
	313	41.0 ± 1.5		
styrene	288	1.36 ± 0.42	14 ± 1	-22 ± 2
	298	3.09 ± 0.09		
	306	5.99 ± 0.24		
	313	10.9 ± 0.4		
norbornene	288	4.70 ± 0.16	14 ± 1	-20 ± 2
	298	9.87 ± 0.32		
	306	21.0 ± 0.7		
	313	36.3 ± 1.4		

stilbene was found to react with *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺ to give a mixture of *cis*- and *trans*-stilbene oxides as well as benzaldehyde.⁹

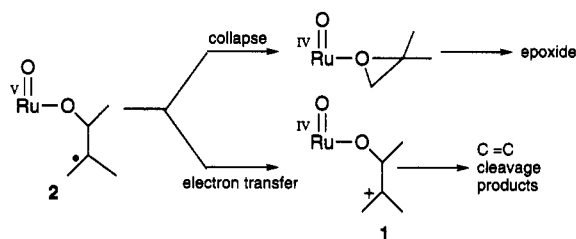
In view of the small $E_{1/2}$ value for the Ru(VI)/Ru(V) couple of *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺ (0.53V vs Ag/AgNO₃), an outersphere one-electron transfer mechanism is excluded because the one-electron oxidation potentials of alkenes chosen in this study are much greater than the ruthenium couple. Because of the large and negative ΔS^\ddagger values, preassociation of reactants must take place prior to oxidation. Three possible pathways are proposed and depicted in Scheme 3. Scheme 3 includes electrophilic attack by *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺ on the alkene to give an acyclic metal-oxo carbocation (1) (pathway d), acyclic metal-oxo carbon radical (pathway e), or a cage pair (3) consisting of alkene-derived carbocation radical and *cis*-[Ru^V(Tet-Me₆)O₂]⁺ (pathway f). The intermediates 2 and 3 may undergo internal electron transfer to give (1) which collapses to give the oxidation products.

The carbocation radical 3 formed via pathway f is prone to rearrangement. This is the case for oxidation of norbornene by hypervalent oxometalloporphyrins which give both *exo*- and *endo*-norbornene oxide and other

Scheme 3



Scheme 4



products like norcamphor and cyclohexene-4-carbaldehyde.²⁰ As suggested by Traylor and co-workers, such a finding could be rationalized by pathway f.²¹ In this work, *exo*-norbornene oxide was found to be the exclusive product of oxidation, and this strongly argues against the viability of pathway f.

In the absence of any rate saturation kinetics being observed, both pathways d and e can account for the experimental rate law. The linear dependence of $\log k_{\text{rel}}$ (k_{rel} = relative second-order rate constant) versus σ^+ for the oxidation of *para*-substituted styrenes suggests a conjugation of the α -carbon of styrene with *para*-substituents and a common mechanism operating for all styrenes. The ρ^+ value of -2.0 observed in this study might agree with an electrophilic mechanism with a substantial buildup of positive charge at the α -carbon of styrene in the transition state. However, this value is far too small when compared with the ρ^+ values of, for instance, hydration of alkene²² (-3.58) and bromination of alkene²³ (-4.8), which involve the rate-limiting formation of carbocation. This ρ^+ value is, in fact, similar in magnitude to that of -1.9 for oxidation of substituted styrenes by oxo(porphyrinato)chromium(V).²⁴

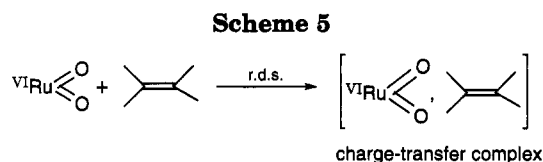
We, therefore, suggest that the oxidation of alkenes by *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺ might proceed via a radical pathway e. The carbon radical 2 could collapse to give epoxides or, as mentioned above, undergo further oxidation to a carbocation 1 which leads to the cleavage products. It is not inconceivable that the *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺ complex has a high propensity to undergo one-electron reduction in aprotic media as exemplified by the isolation of the *cis*-[Ru^V(Tet-Me₆)O₂]⁺ complex after amine reduction in acetone as well as the facile allylic C-H oxidation of cyclohexene to 2-cyclohexenone.⁹

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We do not exclude the possibility that oxidation of alkenes by *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺ proceeds via rate-limiting formation of a charge-transfer complex (Scheme 5). Subsequent reaction via pathway d and/or e could lead to various oxidized products.

General Comments

We found that *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺ is a facile oxidant for alcohols, aromatic hydrocarbons, and alkenes under mild conditions. This is quite different from the corresponding *trans*-dioxoruthenium(VI) complex, *trans*-[Ru^{VI}(14-TMC)O₂]²⁺, which is rather unreactive.^{11b} The kinetic isotopic effects and activation parameters for the oxidation of aromatic hydrocarbons by both *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺ ($k_H/k_D = 11$, $\Delta S^\ddagger = -30$ eu) and *trans*-[Ru^{VI}(L)O₂]²⁺ (L = N₂O₂, pytn) ($k_H/k_D = 12-16$, $\Delta S^\ddagger = -22$ to -24 eu)¹⁸ have been found to be similar. Thus, the reactions could involve substantial C-H bond activation in the transition state, similar to that suggested for the oxidation of *trans*-dioxoruthenium (VI).

The addition of nucleophile has been shown to assist the oxidation of aromatic hydrocarbons by [Ru^{IV}(bpy)₂(py)O]²⁺ (py = pyridine).²⁵ However, in the present study, the rate constants were found to be insensitive to the addition of water or *tert*-butyl alcohol (Table 4). This suggests that either there is no involvement of nucleophile in the rate-determining step or the hydride transfer in Ru(VI) is less sensitive to nucleophilic attack than that in Ru(IV).

Unlike OsO₄, oxidation of alkenes chosen in this work by *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺ did not give any diol, but only epoxide and carbonyl products. Kinetic studies are in favor of a view that oxidation of C=C bond oxidation is

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brought about by an electrophilic attack of the Ru=O moiety, which is similar to that of *trans*-dioxoruthenium(VI) and monooxoruthenium(IV) complexes. As far as alkene epoxidation is concerned, however, monooxoruthenium(IV) complexes are selective oxidants when compared with both *trans*- and *cis*-dioxoruthenium(VI) complexes.²⁶ To account for the cleavage of the C=C bond, the [3 + 2] cycloaddition of *cis*-dioxoruthenium(VI) with alkene to give dioxometallacycle as proposed by Drago and co-workers,¹⁰ is possible. However, no diol product was found, and monooxoruthenium(IV) was found to be the immediate product of reduction.

Interest in *cis*-dioxoruthenium(VI) also stems from the anticipation that these complexes might mimic the reactivity of RuO₄ or OsO₄, where two oxygen atoms could be simultaneously transferred to the same substrate. Thus, they could be a very useful model for the study of the synthetically important *cis*-dihydroxylation reaction. Meyer and co-workers reported a double oxygenation (*four-electron oxidation*) of bis(diphenylphosphino)ethane by a *cis*-directed *trans*-[Ru^{VI}(terpy)(H₂O)O₂]²⁺ (terpy = 2,2':6',2''-terpyridine) in acetonitrile.²⁷ However, the reaction is limited to reactive substrates such as phosphines. Double oxygenation of diphosphine was also observed for *cis*-[Ru^{VI}(Tet-Me₆)O₂]²⁺.²⁸ Attempts to use dimethyl sulfide as the reductant to effect sulfone formation were unsuccessful, producing only dimethyl sulfoxide quantitatively.

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