

# A Mechanistic Investigation of Alkene Epoxidation by Sterically Encumbered *trans*-Dioxoruthenium(VI) Porphyrins

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The highly substituted dioxoruthenium(VI) porphyrins [Ru<sup>VI</sup>(DPP)O<sub>2</sub>] (**1a**; H<sub>2</sub>DPP = 2,3,5,7,8,10,12,13,15,17,18,20-dodecaphenylporphyrin), [Ru<sup>VI</sup>(TDCPP)O<sub>2</sub>] (**1b**; H<sub>2</sub>TDCPP = *meso*-tetrakis(2,6-dichlorophenyl)porphyrin), and [Ru<sup>VI</sup>(TMOPP)O<sub>2</sub>] (**1c**; H<sub>2</sub>TMOPP = *meso*-tetrakis(2,4,6-trimethoxyphenyl)porphyrin) are competent oxidants for alkene epoxidation. The oxidations were carried out in a CH<sub>2</sub>Cl<sub>2</sub>/Hpz solution, and a paramagnetic bis(pyrazolato)ruthenium(IV) porphyrin, [Ru<sup>IV</sup>(Por)(pz)<sub>2</sub>] (**2**; H<sub>2</sub>Por = H<sub>2</sub>DPP, H<sub>2</sub>TDCPP, H<sub>2</sub>TMOPP), was isolated and characterized. For the oxidation of *cis*-alkenes, stereoselectivity is dependent upon both the alkenes and the ruthenium oxidants, and it decreases in the order: *cis*-stilbene > *cis*- $\beta$ -methylstyrene > *cis*- $\beta$ -deuteriostyrene. The observation of inverse secondary KIE for the oxidation of  $\beta$ -*d*<sub>2</sub>-styrene [ $k_{\text{H}}/k_{\text{D}} = 0.87$  (**1a**); 0.86 (**1b**)] but not for the  $\alpha$ -deuteriostyrene oxidations suggests that the C–O bond formation is more advanced at the C( $\beta$ ) atom than at the C( $\alpha$ ) atom of styrene, consistent with a nonconcerted mechanism. By consideration of spin delocalization and polar effects, the second-order rate constants for the oxidation of para-substituted styrenes by complexes **1a–c** can linearly correlate with the carbocyclic substituent constants  $\sigma_{\text{mb}}$  and  $\sigma_{\text{JJ}}^*$  (Jiang, X.-K. *Acc. Chem. Res.* **1997**, *30*, 283). This implies that the styrene oxidation by the dioxoruthenium(VI) porphyrins should involve rate-limiting generation of a benzylic radical intermediate, and the magnitude of  $|\rho_{\text{JJ}}^*/\rho_{\text{mb}}| > 1$  suggests that the spin delocalization effect is more important than the polar effect in the epoxidation reactions. The spontaneous epoxidation of *trans*- $\beta$ -methylstyrene by the sterically encumbered [Ru<sup>VI</sup>(TDCPP)O<sub>2</sub>] and [Ru<sup>VI</sup>(TMOPP)O<sub>2</sub>] complexes and the comparable  $\Delta S^\ddagger$  values for their reactions with *trans*- $\beta$ -methylstyrene and styrene are incompatible with the “side-on approach” model; a “head-on approach” model is implicated.

## Introduction

Metalloporphyrin-catalyzed alkene epoxidations and alkane hydroxylations have been widely invoked as the biomimetic reactions of cytochrome P450.<sup>1</sup> These reactions are often characterized by remarkable regio- and stereoselectivities, and systematic structural variation of the porphyrin ligands has proved to be a useful strategy to achieve electronic and steric tuning of the catalysts.<sup>2</sup> Highly enantioselective epoxidation of unfunctionalized alkenes relying solely on nonbonding interactions has also been developed by using chiral metalloporphyrin catalysts.<sup>3,4</sup> Reactive metal–oxo (M=O) complexes are often invoked as reactive intermediates in the metalloporphyrin-catalyzed organic oxidations,<sup>2,5</sup> and isolation and/or characterization of some oxometalloporphyrin complexes of Cr, Mn, and Fe have been reported.<sup>6</sup> The structure–reactivity relationship of reactive oxometal-

loporphyrin complexes, however, remains less understood. Toward this end, our approach is to scrutinize closely the stoichiometric reactions of organic substrates with well-characterized and highly reactive oxo–metal complexes.<sup>7–12</sup>

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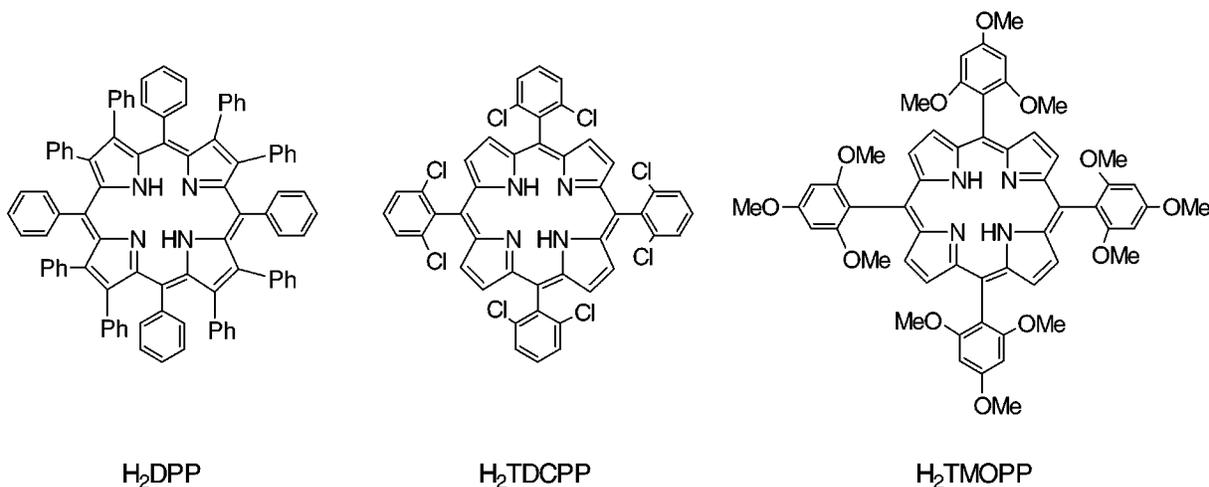
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**Figure 1.**

Recently, ruthenium porphyrins were shown to exhibit excellent activities and selectivities for catalytic hydrocarbon oxidations in homogeneous<sup>13–16</sup> and heterogeneous<sup>17</sup> conditions using mild and inexpensive oxidants such as N<sub>2</sub>O,<sup>15</sup> 2,6-dichloropyridine *N*-oxide,<sup>15</sup> and O<sub>2</sub>.<sup>4a,16</sup> More importantly, high-valent dioxoruthenium(VI) porphyrin complexes can be isolated and have been found to be competent oxidants for hydrocarbon oxidations.<sup>18</sup> We previously prepared two dioxoruthenium(VI) complexes of tetraphenylporphyrin (H<sub>2</sub>TTP) and 2,3,7,8,12,13,17,18-octaethylporphyrin (H<sub>2</sub>OEP),<sup>18b</sup> and they can bring about selective alkene epoxidations and saturated C–H bond oxidations.<sup>7b</sup> Kinetic studies revealed that the oxidation reactions involve the rate-limiting association of oxoruthenium and substrates. This suggests that it is possible to exercise regio- and stereocontrol of the reactions by introducing bulky substituents near the O=Ru moiety. As anticipated, a well-characterized [Ru<sup>VI</sup>(D<sub>4</sub>-Por\*)O<sub>2</sub>] complex [D<sub>4</sub>-H<sub>2</sub>Por\* = 5,10,15,20-tetrakis-(1*S*,4*R*,5*R*,8*S*-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracen-9-yl)porphyrin] was found to effect enantioselective epoxidation of styrene and derivatives in up to 70% ee.<sup>4a,b</sup> To further investigate the role of sterically encumbered porphyrins in the oxidation chemistry of oxometalporphyrins, we have prepared and examined the reactivities of a series of dioxoruthenium(VI) complexes supported by highly substituted porphyrins (Figure 1), [Ru<sup>VI</sup>(DPP)O<sub>2</sub>] (**1a**; H<sub>2</sub>DPP = 2,3,5,7,8,10,12,13,15,17,18,20-dodecaphenylporphyrin), [Ru<sup>VI</sup>(TDCPP)O<sub>2</sub>] (**1b**; H<sub>2</sub>TDCPP = *meso*-tetrakis(2,6-dichlorophenyl)por-

phyrin), and [Ru<sup>VI</sup>(TMOPP)O<sub>2</sub>] (**1c**; H<sub>2</sub>TMOPP = *meso*-tetrakis(2,4,6-trimethoxyphenyl)porphyrin). The porphyrin macrocycle of [Ru<sup>VI</sup>(DPP)O<sub>2</sub>] is saddle-shaped distorted as a result of steric interaction among the phenyl substituents; preliminary studies on its preparation and reactivities have been reported.<sup>18d</sup> The facile oxidation of *trans*- $\beta$ -methylstyrene by the bulky [Ru<sup>VI</sup>(TDCPP)O<sub>2</sub>] and [Ru<sup>VI</sup>(TMOPP)O<sub>2</sub>] complexes are incompatible with the commonly accepted “side-on approach” model for the metalloporphyrin-catalyzed epoxidations, and a “head-on approach” model is implicated.

## Results and Discussion

**Preparation and Characterization of [Ru<sup>VI</sup>(Por)-O<sub>2</sub>] (H<sub>2</sub>Por = H<sub>2</sub>DPP, H<sub>2</sub>TDCPP, and H<sub>2</sub>TMOPP).** The dioxoruthenium(VI) porphyrins were prepared by the oxidation of the ruthenium(II) carbonyl porphyrins in methylene chloride using *m*-chloroperoxybenzoic acid. After chromatographic purification on an alumina column using CH<sub>2</sub>Cl<sub>2</sub> as the eluant, the complexes were isolated in ca. 75% yield. The <sup>1</sup>H NMR spectra of the [Ru<sup>VI</sup>(Por)-O<sub>2</sub>] products are typical of a D<sub>4</sub>-symmetric diamagnetic complex, and the diamagnetism is in agreement with a singlet (d<sub>xy</sub>)<sup>2</sup> electronic ground state (considering O=Ru=O axis as the *z*-direction). The eight pyrrolic protons of [Ru<sup>VI</sup>(TMOPP)O<sub>2</sub>] (**1c**) are located at  $\delta_{\text{H}} = 8.97$  ppm. Infrared analyses of the complexes revealed intense absorptions at 818 (**1a**), 825 (**1b**), and 820 (**1c**) cm<sup>-1</sup> assignable as the asymmetric O=Ru=O stretches, and the oxidation state marker bands are located at 1012 (**1a**), 1019 (**1b**), and 1018 (**1c**) cm<sup>-1</sup> in accord with a Ru(VI) formulation. The UV–vis spectra of [Ru<sup>VI</sup>(Por)O<sub>2</sub>] are characterized mainly by the Soret band (B band) and a less intense Q-band typical of a normal porphyrin.<sup>18</sup> As noted earlier, both the Soret and Q-bands of [Ru<sup>VI</sup>(DPP)-O<sub>2</sub>] were found to be red-shifted compared to those of the planar [Ru<sup>VI</sup>(TPP)O<sub>2</sub>] analogue;<sup>18d</sup> the steric-induced macrocyclic distortion has led to a larger destabilization of the ligand's HOMOs than of its LUMOs, thereby narrowing the HOMO–LUMO gap.<sup>19,20</sup>

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Table 1. Stoichiometric Alkene Oxidations by Dioxoruthenium(VI) Porphyrins

			$\text{CH}_2\text{Cl}_2$ $\xrightarrow[\text{Hpz (2\%w/w)}]{[\text{Ru}^{\text{VI}}(\text{Por})\text{O}_2]}$								
			$\text{[Ru}^{\text{IV}}(\text{Por})(\text{pz})_2]$								
			$\text{H}_2\text{Por} = \text{H}_2\text{DPP (a)}$ $= \text{H}_2\text{TDCPP (b)}$ $= \text{H}_2\text{TMOPP (c)}$								
			%yield <sup>a</sup>								
entry	alkene	products	(1a)	(1b)	(1c)	entry	alkene	products	(1a)	(1b)	(1c)
1			>99 <sup>b</sup> (95) <sup>d</sup>	91 <sup>b</sup> (90) <sup>d</sup>	69 <sup>b</sup> (71) <sup>d</sup>	6			89	81	50
2			82	79	48	7			5	5	12
		acetophenone	6	6	8	8			>99 (>99) <sup>d</sup>	>99 (>99) <sup>d</sup>	73 (74) <sup>d</sup>
3			99	77	46	9			55	55	40
		PhCHO	trace	trace	7				27	28	19
4			85	84	58				14	12	10
			14	n.d.	n.d.				trace	trace	trace
		PhCHO	trace	trace	9	10			80	33	24
5			61	87	62				3	11	18
			39	13	14				14	30	9

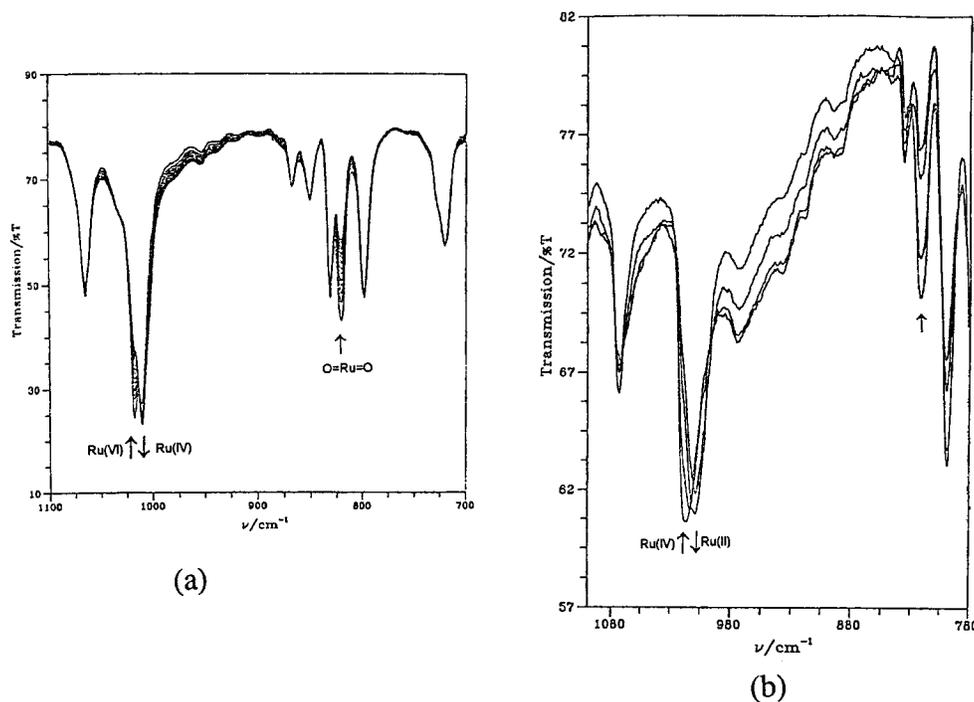
Reaction conditions: To a degassed  $\text{CH}_2\text{Cl}_2$  solution (5 mL) containing Hpz (2 %w/w) and alkenes (2mmol) was added  $[\text{Ru}^{\text{VI}}(\text{Por})\text{O}_2]$  (30  $\mu\text{mol}$ ) under an argon atmosphere. After stirring for 12 h at room temperature, the reaction mixture was filtered through an alumina column with a hexanes-ethyl acetate (9 : 1) mixture as the eluant. The organic products were then analyzed and quantified by either GC or  $^1\text{H}$  NMR using the internal standard method. <sup>a</sup>: Yields are based on the ruthenium oxidant used. <sup>b</sup>: Trace amount of benzaldehyde was detected. <sup>c</sup>: n.d. = Not detected. <sup>d</sup>: An excess of EtOH was used instead of Hpz

**Alkene Oxidations by *trans*-Dioxoruthenium(VI) Porphyrins and the Isolation of the Bis(pyrazolato)ruthenium(IV) Porphyrins.** The  $[\text{Ru}^{\text{VI}}(\text{Por})\text{O}_2]$  complexes **1a–c** are competent oxidants for alkene oxidations at ambient conditions. The results of the stoichiometric oxidations are depicted in Table 1. In a typical reaction, styrene (2 mmol) in a degassed  $\text{CH}_2\text{Cl}_2$  solution [3 mL, containing 2% w/w pyrazole (Hpz)] was treated with  $[\text{Ru}^{\text{VI}}(\text{Por})\text{O}_2]$  (30  $\mu\text{mol}$ ) at room temperature, and the mixture was stirred for 12 h. Styrene oxide was produced in >90% yield for **1b** and **1c**. A trace amount of benzaldehyde (C=C bond cleavage) was also formed, and phenylacetaldehyde (rearrangement) was not detected (entry 1). At the end of the reactions, a bis(pyrazolato)ruthenium(IV) porphyrin complex,  $[\text{Ru}^{\text{IV}}(\text{Por})(\text{pz})_2]$  (**2**), was isolated and characterized. The molecular structure of  $[\text{Ru}^{\text{IV}}(\text{DPP})(\text{pz})_2]$  (**2a**) had previously been established by X-ray diffraction method.<sup>18d</sup> The  $[\text{Ru}^{\text{IV}}(\text{Por})(\text{pz})_2]$  complexes are paramagnetic, and the effective magnetic moments ( $\mu_{\text{eff}}$ ) were measured to be 3.24 (**2a**), 2.68 (**2b**) and 2.88  $\mu_{\text{B}}$  (**2c**) (for spectral characterization data, see the Experimental Section for details), consistent with the Ru(IV) formulation.<sup>21</sup>

In a  $\text{CH}_2\text{Cl}_2$ /ethanol mixture, the  $[\text{Ru}^{\text{VI}}(\text{Por})\text{O}_2]$  complexes reacted with norbornene or styrene to afford the epoxides in comparable yields (see Table 1, entries 1 and 7) as in the cases when excess Hpz was used. However, dark precipitates that are insoluble in common organic solvents were formed at the end of the reactions. Infrared spectral analyses of these solids did not reveal the asymmetric O=Ru=O stretch, and a distinct absorption around 1010  $\text{cm}^{-1}$  was readily assignable as the oxidation marker band of Ru(IV) porphyrins. Assuming a  $[\text{Ru}(\text{Por})(\text{OEt})_2]$  formulation,<sup>21c</sup> their effective magnetic moments were evaluated as 2.6–2.8  $\mu_{\text{B}}$  (solid sample).

In the absence of Hpz or ethanol, the reaction of  $[\text{Ru}^{\text{VI}}(\text{TDCPP})\text{O}_2]$  (**1b**) with excess norbornene in  $\text{CH}_2\text{Cl}_2$  was monitored by infrared spectroscopy (1100–780  $\text{cm}^{-1}$ ). The intensities of the oxidation state marker band (1019  $\text{cm}^{-1}$ ) and the asymmetric O=Ru=O stretch (825  $\text{cm}^{-1}$ ) of the starting Ru(VI) complex decreased isosbastically over 0.5 h with a concurrent development of an intense absorption at 1010  $\text{cm}^{-1}$ , i.e., the formation of a Ru(IV) porphyrin complex (Figure 2a). Upon prolonged standing of the reaction mixture, this spectral feature was subsequently replaced by a new absorption band at 1007  $\text{cm}^{-1}$  assignable to the oxidation marker band of a Ru(II) porphyrin complex (Figure 2b). The result is consistent with the findings by Groves and co-workers that oxoruthenium(IV) porphyrin intermediate is unstable toward disproportionation into Ru(VI) and Ru(II).<sup>22</sup> Indeed, without excess pyrazole or ethanol, the norbornene and cy-

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**Figure 2.** Infrared spectral traces for norbornene oxidation by  $[\text{Ru}^{\text{VI}}(\text{TDCPP})\text{O}_2]$  ( $1100\text{--}780\text{ cm}^{-1}$ ): (a) first 30 min of the reaction and (b) over 14 h of prolonged standing of the reaction mixture. The absorption bands due to norbornene and  $\text{CH}_2\text{Cl}_2$  have been subtracted.

clooctene oxidations by 1 equiv of  $[\text{Ru}^{\text{VI}}(\text{TDCPP})\text{O}_2]$  in degassed benzene gave 2 equiv of *exo*-2,3-epoxynorbornane and 1.4 equiv of cyclooctene oxide, respectively. Under such conditions, a carbonylruthenium(II) porphyrin ( $\nu_{\text{CO}} = 1950\text{ cm}^{-1}$ ) and some unidentified ruthenium complexes were isolated at the end of the reactions.

#### Product Analysis and Kinetic Measurements.

Styrene, norbornene, and cyclooctene were converted to the corresponding epoxides by **1a** and **1b** in 71–99% yields, whereas lower epoxide yields (70–50%) were obtained when **1c** was used as the oxidant (Table 1, entries 1, 7, and 8, respectively). Allylic C–H bond oxidation prevailed for the cyclohexene oxidations by  $[\text{Ru}^{\text{VI}}(\text{Por})\text{O}_2]$ , and the combined yields of 2-cyclohexen-1-ol and 2-cyclohexen-1-one were 83% (**1a**), 44% (**1b**), and 42% (**1c**) (see entry 10).

All of the dioxoruthenium(VI) porphyrins studied here are unreactive to *trans*-stilbene oxidation; however, they readily oxidized *trans*- $\beta$ -methylstyrene to afford *trans*-epoxide selectively (entry 6). The *cis*-stilbene oxidations by **1a–c** were found to be highly stereoretentive (entry 3). In contrast, the stereoselectivity of the *cis*- $\beta$ -methylstyrene oxidation varies with the nature of the ruthenium oxidants. For example, when  $[\text{Ru}^{\text{VI}}(\text{TDCPP})\text{O}_2]$  (**1b**) and  $[\text{Ru}^{\text{VI}}(\text{TMOPP})\text{O}_2]$  (**1c**) reacted with *cis*- $\beta$ -methylstyrene, only *cis*- $\beta$ -methylstyrene oxide was produced in 84% and 58% yields, respectively. On the other hand, a significant amount of the *trans*- $\beta$ -methylstyrene oxide (14%) along with the *cis*-epoxide (85%) were found when  $[\text{Ru}^{\text{VI}}(\text{DPP})\text{O}_2]$  (**1a**) was the oxidant (entry 4).

When (+)-limonene containing an internal trisubstituted and an isolated terminal C=C bond reacted with the dioxoruthenium(VI) complexes, 1,2-epoxides were selectively produced and only a trace amount of 8,9-epoxide was detected (entry 9), i.e.,  $[\text{Ru}^{\text{VI}}(\text{Por})\text{O}_2]$  pref-

erentially acts on the trisubstituted C=C bond. It is known that the (+)-limonene oxidation by *m*-chloroperoxybenzoic acid would furnish a mixture of 1,2- and 8,9-epoxides (ratio = 8.9:1),<sup>23</sup> and the reaction would result in an equimolar amount of *cis*- and *trans*-1,2-epoxides nonstereoselectively.<sup>23</sup> In this work, we found that the stoichiometric (+)-limonene oxidations by the dioxoruthenium(VI) porphyrins afforded *cis*-1,2-epoxide as the major product; *cis*:*trans*-epoxide ratios = 55:27 (**1a**), 55:28 (**1b**), and 40:19 (**1c**) (see entry 9). The observed stereoselectivity is indeed not inconceivable because the facial approach leading to *trans*-1,2-epoxide is more hindered as a result of the steric interaction between the vinyl groups of the alkene and the substituents on the porphyrin ring of the ruthenium complexes.

Figure 3 depicts the UV–vis spectral change for the styrene oxidation by  $[\text{Ru}^{\text{VI}}(\text{TDCPP})\text{O}_2]$  (**1b**) in  $\text{CH}_2\text{Cl}_2$  with 2% w/w pyrazole showing the isobestic transformation from Ru(VI) to a Ru(IV) porphyrin (**2b**). Similar spectral features were also observed for the reactions involving the other dioxoruthenium(VI) porphyrin complexes **1a** and **1c**. Isobestic points were located at 431 and 468 nm for **1a** (411 and 435 nm for **1b** and 415 and 442 nm for **1c**), suggesting that Hpz can spontaneously react with the putative Ru(IV)–oxo intermediates to form  $[\text{Ru}^{\text{VI}}(\text{Por})(\text{pz})_2]$  without accumulation of intermediates. For the styrene oxidation by  $[\text{Ru}^{\text{VI}}(\text{DPP})\text{O}_2]$  and  $[\text{Ru}^{\text{VI}}(\text{TDCPP})\text{O}_2]$ , ethanol was found to be equally effective as Hpz for obtaining clean isobestic spectral changes. However, without pyrazole, the reaction involving the less reactive  $[\text{Ru}^{\text{VI}}(\text{TMOPP})\text{O}_2]$  displayed complicated kinetics in a  $\text{CH}_2\text{Cl}_2/\text{EtOH}$  mixture. It should be noted that the reactions of all of the olefinic substrates utilized

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**Table 2. Second-Order Rate Constants ( $k_2$ ) for the Oxidation of Alkenes by Dioxoruthenium(VI) Porphyrins**

entry	alkenes	$k_2 \times 10^3$ (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )		
		<b>1a</b>	<b>1b</b>	<b>1c</b>
1	styrene	4.78 ± 0.11	3.90 ± 0.14 (3.63 ± 0.12) <sup>a</sup>	0.61 ± 0.03 (0.50 ± 0.01) <sup>a</sup>
2	4-methoxystyrene	25.2 ± 1.2	18.8 ± 1.1	5.77 ± 0.14
3	4-methylstyrene	10.0 ± 0.4	8.6 ± 0.2	1.70 ± 0.06
4	4-fluorostyrene	6.01 ± 0.14	5.06 ± 0.18	1.01 ± 0.06
5	4-chlorostyrene	6.78 ± 0.18	5.72 ± 0.15	1.26 ± 0.06
6	3-nitrostyrene	5.55 ± 0.17	5.18 ± 0.16	1.34 ± 0.08
7	<i>cis</i> - $\beta$ -methylstyrene	3.28 ± 0.18	3.40 ± 0.14	0.57 ± 0.03
8	<i>trans</i> - $\beta$ -methylstyrene	2.59 ± 0.12	1.69 ± 0.08	0.46 ± 0.02
9	$\alpha$ -methylstyrene	2.07 ± 0.10	1.44 ± 0.07	0.39 ± 0.02
10	norbornene	3.76 ± 0.14	12.7 ± 0.6 (15.0 ± 0.05) <sup>a</sup>	0.87 ± 0.041 (0.53 ± 0.03) <sup>a</sup>
11	<i>cis</i> -stilbene	1.73 ± 0.06	1.77 ± 0.09	0.19 ± 0.01
12	cyclooctene	1.89 ± 0.06	1.21 ± 0.06 (1.04 ± 0.04) <sup>a</sup>	0.29 ± 0.02 (0.22 ± 0.01) <sup>a</sup>
13	$\beta$ - <i>d</i> <sub>2</sub> -styrene	5.49 ± 0.13	4.53 ± 0.12	
14	$\alpha$ -deuteriostyrene	4.74 ± 0.11	3.86 ± 0.13	

<sup>a</sup> The values in parentheses were obtained when the kinetic experiments were conducted in a CH<sub>2</sub>Cl<sub>2</sub>/EtOH mixture at 298 K.

**Table 3. Activation Parameters for the Oxidation of Styrene, *cis*- $\beta$ -Methylstyrene, *trans*- $\beta$ -Methylstyrene, and Norbornene**

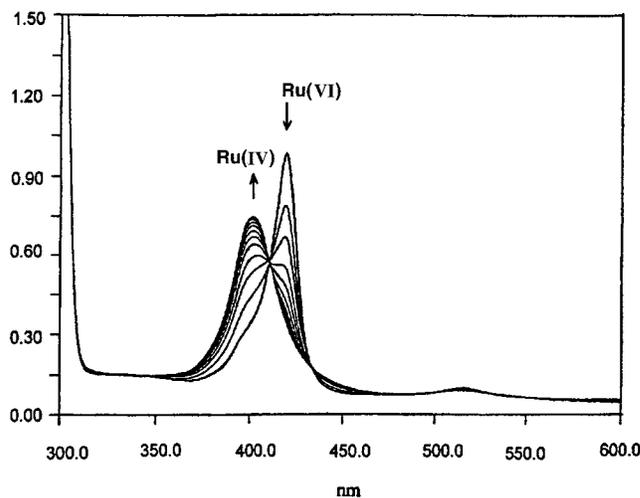
alkenes	<b>1a</b>		<b>1b</b>		<b>1c</b>	
	$\Delta H^\ddagger$ (kcal mol <sup>-1</sup> )	$\Delta S^\ddagger$ (eu)	$\Delta H^\ddagger$ (kcal mol <sup>-1</sup> )	$\Delta S^\ddagger$ (eu)	$\Delta H^\ddagger$ (kcal mol <sup>-1</sup> )	$\Delta S^\ddagger$ (eu)
styrene	14.6 ± 1.0	-(20.1 ± 2.0)	14.3 ± 1.0	-(21.9 ± 2.3)	14.0 ± 1.4	-(27.3 ± 2.8)
norbornene	13.3 ± 1.0	-(25.0 ± 2.2)	13.2 ± 1.0 <sup>a</sup>	-(25.6 ± 2.6) <sup>a</sup>	13.4 ± 1.2 <sup>a</sup>	-(29.0 ± 2.7) <sup>a</sup>
			11.8 ± 1.0	-(27.6 ± 2.1)	12.2 ± 0.9	-(31.6 ± 2.4)
<i>cis</i> - $\beta$ -methylstyrene			12.2 ± 1.0 <sup>a</sup>	-(26.1 ± 1.9) <sup>a</sup>		
<i>trans</i> - $\beta$ -methylstyrene			11.2 ± 0.9	-(32.4 ± 2.8)	13.8 ± 1.2	-(27.3 ± 2.0)
			14.3 ± 1.2	-(23.7 ± 2.5)	14.5 ± 0.9	-(23.7 ± 2.8)

<sup>a</sup> The kinetic experiments were conducted in a CH<sub>2</sub>Cl<sub>2</sub>/EtOH solvent.

here, para-substituted styrenes,  $\alpha$ -methylstyrene, *cis*- and *trans*- $\beta$ -methylstyrenes, and norbornene, exhibited isobestic spectral changes and followed clean first-order kinetics under pseudo-first-order conditions, i.e., [alkene]  $\gg$  [Ru], in a CH<sub>2</sub>Cl<sub>2</sub> / 2% w/w Hpz solution.

The pseudo-first-order rate constants,  $k_{\text{obs}}$ , were determined by monitoring the disappearance of the Soret band of the dioxoruthenium(VI) complexes in CH<sub>2</sub>Cl<sub>2</sub> with 2% w/w Hpz;  $\lambda_{\text{max}} = 448$  nm for **1a**, 420 nm for **1b**, and 424 nm for **1c**. On the basis of the proposed reaction in Scheme 1, the second-order rate constants,  $k_2$  (see Table 2), were evaluated from the linear plots of  $k_{\text{obs}}$  versus [alkene]. Rate saturation was not observed over the alkene concentrations employed in this work. It is noteworthy that all of the  $k_2$  values were unaffected by changing the amount of Hpz from 1% to 10% w/w in CH<sub>2</sub>Cl<sub>2</sub>. Indeed, comparable  $k_2$  values were obtained for the styrene, norbornene, and cyclooctene oxidations by [Ru<sup>VI</sup>(TDCPP)O<sub>2</sub>] (**1b**) and [Ru<sup>VI</sup>(TMOPP)O<sub>2</sub>] (**1c**) at 298 K, regardless of employment of either the Hpz/CH<sub>2</sub>Cl<sub>2</sub> or EtOH/CH<sub>2</sub>Cl<sub>2</sub> conditions (see Table 2). These verify that Hpz or EtOH does not interfere with the rate-limiting step of the epoxidation reactions.

The temperature effect on the  $k_2$  values for the oxidation of some representative alkenes has been studied. The Eyring plots are linear over a temperature range of 19–42 °C. The activation enthalpies  $\Delta H^\ddagger$  and entropies  $\Delta S^\ddagger$  for the styrene, *trans*- $\beta$ -methylstyrene, *cis*- $\beta$ -methylstyrene, and norbornene oxidations by **1a–c** are shown in Table 3. For the oxidation of styrene and norbornene, small variations of the  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  values were noted upon changing the solvent system from CH<sub>2</sub>Cl<sub>2</sub>/Hpz to CH<sub>2</sub>Cl<sub>2</sub>/EtOH. The large and negative  $\Delta S^\ddagger$  values for the

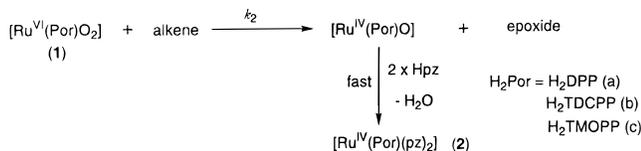


**Figure 3.** UV-vis spectral trace (300–600 nm) for the reaction of styrene (1.0 M) with [Ru<sup>VI</sup>(TDCPP)O<sub>2</sub>] (**1b**) (10  $\mu$ M) in CH<sub>2</sub>Cl<sub>2</sub> (with 2% w/w Hpz) at room temperature. Scan interval: 2 min.

stoichiometric alkene epoxidations are consistent with association of the reactants in the transition states.

**Cis–Trans Alkene Selectivity of Sterically Encumbered Dioxoruthenium(VI) Porphyrins—“Side-On” versus “Head-On” Approach.** Stereoselective *cis*-alkene oxidation is well documented for the metalloporphyrin-catalyzed epoxidations,<sup>2a</sup> and a side-on approach of alkene to a putative oxo–metal complex was first proposed by Groves and co-workers.<sup>3a,23a</sup> This olefinic approach is believed to be favored by a more effective interaction between the filled  $\pi$ -orbital of alkene and the  $d_{\pi-p_{\pi}}$  M–O antibonding orbitals. Later, Groves had

### Scheme 1. Oxidation of Alkenes by Dioxoruthenium(VI) Porphyrins

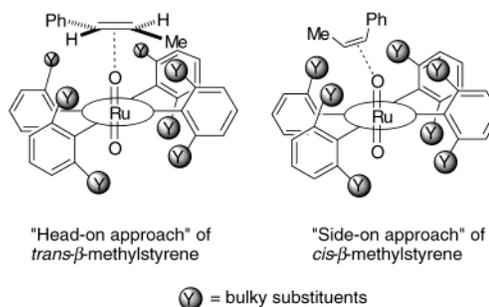


employed the molecular structure of  $[\text{Ru}^{\text{II}}(\text{TDCPP})(\text{CO})\text{-(styrene oxide)}]$  complex, wherein the bound epoxide was inclined at a  $49^\circ$  angle with respect to the mean porphyrinato plane, to model the transition state stereochemistry of the epoxidation.<sup>24</sup> From the X-ray structure, a close nonbonding interaction was noted between the epoxide protons and the porphyrin ring, as well as between the phenyl carbons of the styrene oxide and one of the *ortho*-chloro substituents. It was, therefore, purported that the porphyrin cavity encircled by the chlorine atoms would not have enough room to accommodate a *trans*-1,2-disubstituted epoxide. This deliberation was supported by the failure of *trans*- $\beta$ -methylstyrene oxide to coordinate effectively to bulky ruthenium(II) porphyrins.<sup>24</sup> Indeed, the side-on approach model has gained a widespread acceptance in the oxidation chemistry of metalloporphyrins and has been successfully applied to explain the enantioselectivity of the chiral Mn(salen)-catalyzed asymmetric epoxidation of unfunctionalized alkenes.<sup>25</sup>

To test the generality of the side-on approach as a transition state model for the oxometalloporphyrin-mediated epoxidations, we examined the reactions of two sterically congested dioxoruthenium(VI) porphyrins,  $[\text{Ru}^{\text{VI}}(\text{TDCPP})\text{O}_2]$  (**1b**) and  $[\text{Ru}^{\text{VI}}(\text{TMOPP})\text{O}_2]$  (**1c**), with *cis*- and *trans*- $\beta$ -methylstyrenes. The bulky *ortho* substituents would prevent a side-on approach of the *trans*-alkene to the O=Ru moiety. Therefore, if the side-on approach is an obligatory route for epoxidation, the encumbered dioxoruthenium(VI) porphyrins **1b** and **1c** would be inactive toward *trans*- $\beta$ -methylstyrene oxidation. And yet, in this work, we found that the *cis*- and *trans*-alkenes were readily epoxidized by both ruthenium oxidants to give the corresponding epoxides stereoselectively (see Table 1, entry 6). Furthermore, the  $\Delta S^\ddagger$  values for their reactions with styrene ( $-21.9$  eu for **1b** and  $-27.3$  eu for **1c**) and *trans*- $\beta$ -methylstyrene ( $-23.7$  eu for **1b** and **1c**) are comparable (see Table 3), indicative of a similar degree of oxidant-alkene association in the transition states for the styrene and *trans*- $\beta$ -methylstyrene oxidations. Indeed, the facile oxidation of the *trans*-alkene by the bulky dioxoruthenium(VI) porphyrins cannot be rationalized by the side-on approach model.

Apart from electronic effect, steric hindrance by the bulky substituents had been shown to play an important role in determining the optimal angles of approach of the C=C bond to the Cr<sup>V</sup>=O moiety on the basis of the detailed docking studies on the approach of several *cis*- and *trans*-alkenes to  $[(\text{Br}_8\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})]$  ( $\text{H}_2(\text{Br}_8\text{TPP}) = \text{meso-tetrakis}(2,6\text{-dibromophenyl})\text{porphyrin}$ ) by Bruce and co-workers.<sup>26</sup> For the *trans*- $\beta$ -methylstyrene oxidation

### Scheme 2. "Head-On Approach" Model for the Oxidation of *trans*- $\beta$ -Methylstyrene by Sterically Encumbered Dioxoruthenium(VI) Porphyrins



by the oxochromium(V) porphyrin, the C=C bond would be directed preferably from the top of the Cr<sup>V</sup>=O group. A similar head-on approach model can be implicated to rationalize the facile *trans*- $\beta$ -methylstyrene oxidations by the sterically encumbered  $[\text{Ru}^{\text{VI}}(\text{TDCPP})\text{O}_2]$  and  $[\text{Ru}^{\text{VI}}(\text{TMOPP})\text{O}_2]$  complexes (Scheme 2).<sup>4c</sup>

**Concerted versus Nonconcerted Mechanism.** *cis*-Alkenes have been widely employed as mechanistic probes for the concertedness of oxo-metal-mediated epoxidation reactions.<sup>27</sup> If the epoxidation of *cis*-alkene involves breakage of the C=C  $\pi$  bond resulting in the formation of an acyclic intermediate, i.e., a nonconcerted pathway, then isomerization via the unhindered C-C bond rotation to form the *trans*-epoxide product would occur. In the case of *cis*-stilbene oxidation, the supposed acyclic intermediate is particularly prone to *cis*-*trans* isomerization because of severe steric interaction between the two phenyl rings. In this work, the reactions of **1a-c** with *cis*-stilbene were found to be highly stereoretentive with no detectable formation of *trans*-epoxide. *cis*-Stilbene oxide was formed in 99% and 77% yield for **1a** and **1b** as the oxidants, respectively, whereas a moderate epoxide yield (46%) was obtained for **1c**.

As mentioned earlier, stereospecificities of the *cis*-alkene oxidations were found to vary with both the alkenes and the ruthenium porphyrins. Unlike the *cis*-stilbene oxidations by the sterically congested dioxoruthenium(VI) porphyrins, the analogous reaction with  $[\text{Ru}^{\text{VI}}(\text{OEP})\text{O}_2]$  ( $\text{H}_2\text{OEP} = 2,3,7,8,12,13,17,18\text{-octaethylporphyrin}$ ) afforded *trans*-stilbene oxide as the major product with a *trans*:*cis*-oxide ratio of 44:16.<sup>18b</sup> Although a complete stereoretention was attained for the *cis*- $\beta$ -methylstyrene oxidations by **1b** and **1c**, a substantial amount of *trans*- $\beta$ -methylstyrene oxide (14%) was formed when  $[\text{Ru}^{\text{VI}}(\text{DPP})\text{O}_2]$  (**1a**) was the oxidant.

In this work, the stereoselectivity of the epoxidation reaction was further examined by employing *cis*- $\beta$ -deuteriostyrene as a mechanistic probe.<sup>7e,28</sup> When *cis*- $\beta$ -deuteriostyrene was subjected to the standard reaction conditions, *cis*-alkene (1 mmol),  $[\text{Ru}^{\text{VI}}(\text{Por})\text{O}_2]$  (30  $\mu\text{mol}$ ) in 2% w/w Hpz/ $\text{CH}_2\text{Cl}_2$  under an argon atmosphere, the epoxidation proceeded nonstereospecifically, and the *cis*:*trans*-epoxide ratios were found to be 61:39 (**1a**), 87:13 (**1b**), and 62:14 (**1c**) (see Table 1, entry 5). The oxidations had been repeated three times for each ruthenium oxidant, and the *cis*-*trans* selectivities were obtained in a reproducible manner and reported as average values.

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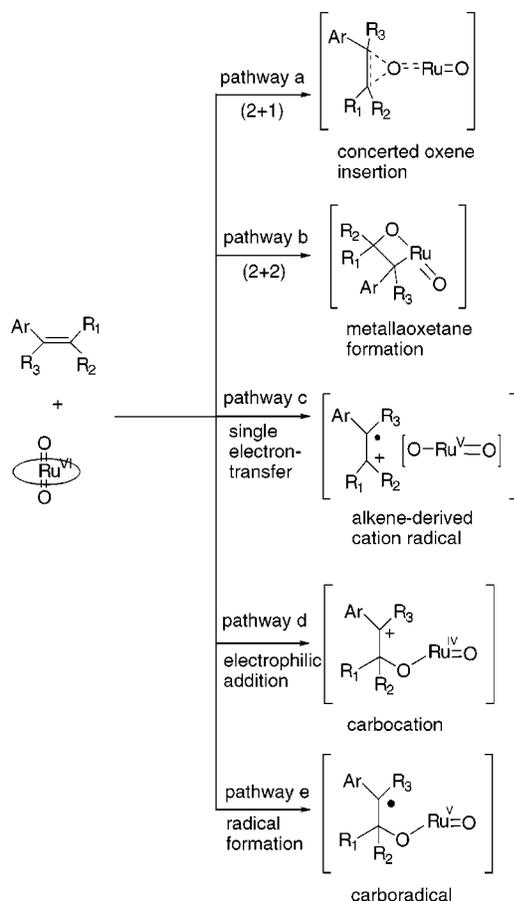
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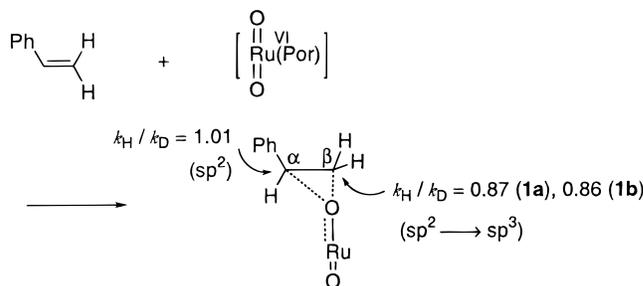
Scheme 3



The purity of *cis*- $\beta$ -deuteriostyrene (>99%) was checked by  $^1\text{H}$  NMR spectroscopy, and the *trans*-alkene was not detected at the end of the reactions. A control experiment was performed by stirring a mixture of pure *cis*- $\beta$ -deuteriostyrene oxide and  $[\text{Ru}^{\text{IV}}(\text{Por})(\text{pz})_2]$  in methylene chloride at room temperature for 12 h, and the starting *cis*-epoxide was fully recovered without *trans*-epoxide being detected. This confirms that the formation of the *cis*- and *trans*-epoxides associated with the *cis*- $\beta$ -deuteriostyrene oxidation did not arise from the Ru-catalyzed epoxide isomerization.<sup>29</sup> Evidently, the loss of stereospecificity is inconsistent with a concerted reaction pathway such as oxene insertion (Scheme 3, pathway a), and a nonconcerted mechanism is more plausible.

The rate-limiting formation of a metallaoxetane intermediate (Scheme 3, pathway b) by (2 + 2) cycloaddition between the  $\text{Ru}=\text{O}$  and  $\text{C}=\text{C}$  bonds is unlikely.<sup>30</sup> This pathway requires the simultaneous rehybridization of both the  $\alpha$ - and  $\beta$ -olefinic carbon atoms from  $\text{sp}^2$  to  $\text{sp}^3$  at the rate-determining step, which is incompatible with the fact that inverse secondary kinetic isotope effect (KIE)<sup>31</sup> has only been observed for the  $\beta$ -*cis*-styrene oxidations ( $k_{\text{H}}/k_{\text{D}} = 0.87$  for **1a** and 0.86 for **1b**) and not for  $\alpha$ -deuteriostyrene ( $k_{\text{H}}/k_{\text{D}} = 1.01$  for **1a** and **1b**); see Table 2 entries 13 and 14. The magnitude of the inverse secondary KIE observed here falls within the 0.82–0.93

Scheme 4. Inverse Secondary KIE for the Oxidation of Styrene



range reported in a related study on asymmetric chiral Mn(salen)-catalyzed alkene epoxidation.<sup>32</sup> The secondary KIE results favor a nonsymmetrical transition state wherein the C–O bond formation is more advanced at the  $\beta$ -carbon atom than at the  $\alpha$ -carbon atom with concomitant rehybridization of the  $\text{C}(\beta)$  atom from  $\text{sp}^2$  to  $\text{sp}^3$ , whereas the latter remains more or less  $\text{sp}^2$  hybridized. It is more consistent with the formation of an acyclic intermediate at the rate-limiting step (Scheme 4). By the same token, the KIE results should also discount a concerted oxene insertion mechanism.

**Nature of Transition State and Hammett Correlation Studies.** The effect of para-substituents on the rate of styrene oxidations by **1a–c** has been investigated (Table 2, entries 1–6). It is noteworthy that both electron-releasing and -withdrawing substituents can moderately accelerate the reactions (~9 to 5-fold for 4-methoxystyrene and 2 to 1.1-fold for 3-nitrostyrene). The correlation of  $\log k_{\text{rel}}$  vs  $\sigma^+$  [ $k_{\text{rel}} = k_2(\text{substituted styrene})/k_2(\text{styrene})$ ] gave rise to concave Hammett curves resembling the cases involving  $[\text{Ru}^{\text{VI}}(\text{TPP})\text{O}_2]^{7b}$  and some cationic oxoruthenium(IV)<sup>7a,e</sup> complexes as oxidants. This is contrary to the linear Hammett  $\log k_{\text{rel}}$  vs  $\sigma^+$  correlations ( $\rho^+ = -1.9$  to  $-2.1$ ) for the styrene oxidations involving the  $[\text{Fe}^{\text{IV}}(\text{TMP}^+)\text{O}]$  ( $\text{H}_2\text{TMP} = \text{tetramesitylporphyrin}$ ),<sup>33</sup>  $[(\text{Br}_3\text{TPP})\text{Cr}^{\text{V}}(\text{O})(\text{X})]$ ,<sup>34</sup> and  $[\text{Ru}^{\text{VI}}(\text{N}_4)\text{O}_2]^{2+}$  ( $\text{N}_4 = \text{macrocyclic tertiary amines}$ )<sup>7c,d</sup> complexes. Because the rate-limiting carbocation formation for the electrophilic addition to the  $\text{C}=\text{C}$  bond would have  $\rho^+$  values as large as  $-3.5$  (hydration)<sup>35</sup> and  $-4.1$  (bromination),<sup>36</sup> the minor influence of the electronic substituent effect on the  $k_2$  values discounts the participation of an alkene-derived cation radical (Scheme 3, pathway c), as well as a carbocation intermediate (Scheme 3, pathway d). The insensitivity of the  $k_2$  values to the para-substituent effect would be more compatible with the rate-limiting formation of a carboradical intermediate (Scheme 3, pathway e).

The alkene-derived cation radical intermediate is expected to be susceptible to skeletal rearrangement. For example, the oxidation of norbornene by some highly oxidizing oxometalloporphyrins produced *exo*- and *endo*-epoxynorbornane, norcamphor, and cyclohexen-4-carboxyaldehyde. A cation radical intermediate was invoked by Traylor and co-workers<sup>37</sup> to explain this finding. In

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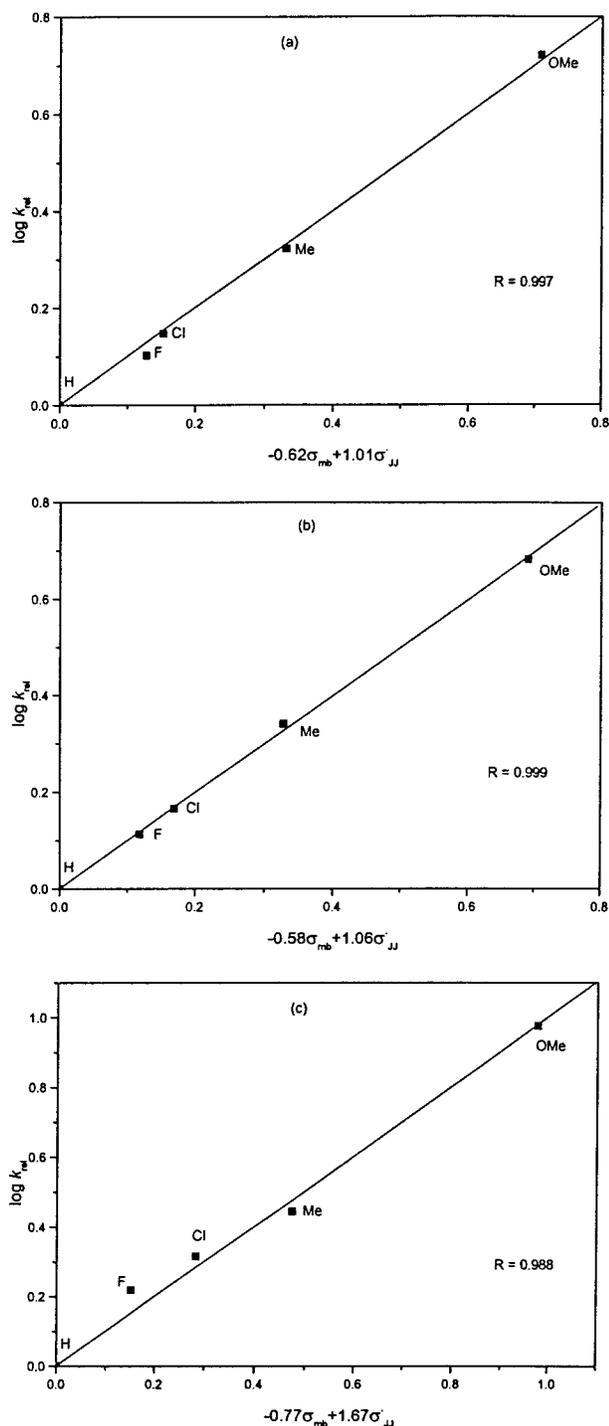
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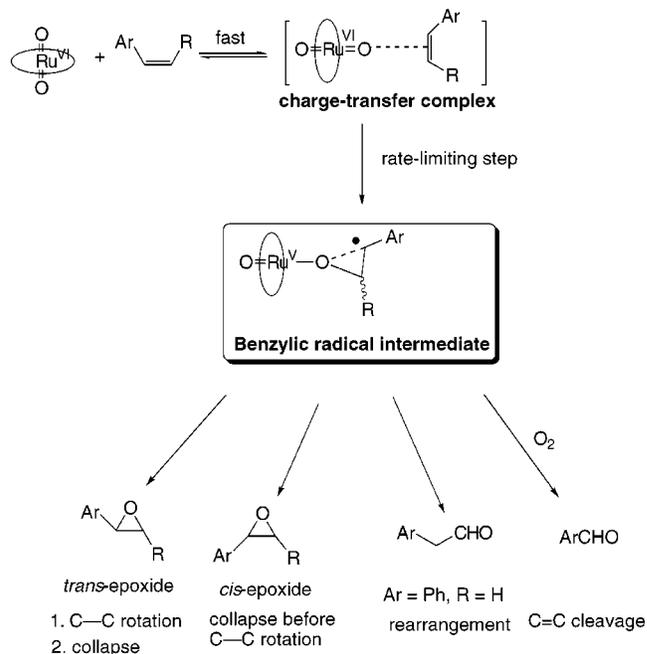
**Figure 4.** Linear dual-parameter Hammett correlations using  $\sigma_{mb}$  and  $\sigma_{JJ^*}$  for the ruthenium oxidation of para-substituted styrenes: (a)  $[\text{Ru}^{\text{VI}}(\text{DPP})\text{O}_2]$ , (b)  $[\text{Ru}^{\text{VI}}(\text{TDCPP})\text{O}_2]$ , and (c)  $[\text{Ru}^{\text{VI}}(\text{TMOPP})\text{O}_2]$ .

this work, *exo*-epoxynorbornane was found to be the exclusive product of the norbornene oxidations (Table 1, entry 7), suggesting that a cation radical species is not necessarily the intermediate of the reaction.

Apart from polar substituent effect, radical reactivity is also influenced by the substituent's ability to delocalize the spin density on the carbon radical center, namely spin delocalization effect. There have been several attempts

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### Scheme 5. Proposed Mechanism for the Oxidation of Alkenes by Dioxoruthenium(VI) Porphyrins



to establish a pure carboradical ( $\sigma^*$ ) substituent constant for spin delocalization effect using spectroscopic and kinetic methods. Notable examples are the works by Arnold ( $\sigma_{\alpha^*}$ ; ESR studies of para-substituted benzylic radicals),<sup>38</sup> Creary ( $\sigma_c^*$ ; kinetic studies of the rearrangement of methylenecyclopropanes),<sup>39</sup> and Jackson ( $\sigma_J^*$ ; kinetic studies of the thermal decomposition of substituted dibenzyl mercurials).<sup>40</sup> However, a complete separation of spin delocalization effect from the residual polar effect was achieved with limited success.

Recently, Jiang and Ji proposed a new carboradical scale,  $\sigma_{JJ^*}$ , based on the kinetic studies of para-substituent effect on thermal cycloaddition reaction of  $\alpha,\beta,\beta$ -trifluorostyrenes.<sup>41</sup> The polar and spin delocalization effects were separated. A substituent constant,  $\sigma_{mb}$ , for the polar effect based on the degree of ground state  $\pi$ -bond polarization induced by the para-substituents was also established. Taking into account the spin delocalization and polar effects, we then applied the  $\sigma_{JJ^*}$  and  $\sigma_{mb}$  substituent constants to our Hammett correlation analysis ( $\log k_{rel} = \rho_{mb}\sigma_{mb} + \rho_{JJ^*}\sigma_{JJ^*}$ ) for the styrene oxidations, and three straight lines resulted (slope = 1.00;  $R = 0.98$ – $0.99$ ) (Figure 4):  $\log k_{rel} = -0.62\sigma_{mb} + 1.01\sigma_{JJ^*}$  (**1a**),  $\log k_{rel} = -0.58\sigma_{mb} + 1.06\sigma_{JJ^*}$  (**1b**), and  $\log k_{rel} = -0.77\sigma_{mb} + 1.67\sigma_{JJ^*}$  (**1c**). The linear Hammett correlations coincide with the rate-determining formation of a benzylic radical intermediate (Scheme 5) for the styrene epoxidations by dioxoruthenium(VI) porphyrins. The positive  $\rho_{JJ^*}$  values suggest that the epoxidation reaction is promoted by delocalizing spin density at the radical center. The negative  $\rho_{mb}$  values are consistent with the electrophilic nature of the oxoruthenium complexes.

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In all three cases, the magnitude of  $|\rho_{JJ^*}/\rho_{mb}| > 1$  suggests that the spin delocalization effect is more important than the polar substituent effect in the dioxoruthenium-mediated alkene epoxidation.<sup>41</sup>

For comparison, we have also applied to our correlation studies another set of carboradical parameters, namely, the total substituent effect (TE) proposed by Wu and co-workers.<sup>42</sup> The parameters were established by the density functional calculation (BLYP/6-31\*) based on the influence of the para-substituents on the benzylic C-H bond dissociation energies of toluenes. It should be noted that the TE parameters reflect the combined substituent effect of the change in spin ( $\Delta s$ ) and charge ( $\Delta c$ ) densities at the radical center:  $TE = -29.9\Delta s - 11.7\Delta c$ , where the spin delocalization effect is dominant. As expected, an excellent linear correlation ( $R = 0.99$ ) between  $\log k_{rel}$  for the substituted styrene oxidations by  $[Ru^{VI}(DPP)O_2]$  (**1a**),  $[Ru^{VI}(TDCPP)O_2]$  (**1b**), and  $[Ru^{VI}(TMOPP)O_2]$  (**1c**) with TE was attained with slopes of  $\rho_{TE^*} = +0.67$ ,  $+0.63$ , and  $+0.86$ , respectively.<sup>43</sup> Analogous to the  $\rho_{JJ^*}$  value, the positive  $\rho_{TE^*}$  values also indicate that the styrene oxidation is promoted by delocalizing spin density on the radical center. Indeed, the results of the correlation analyses based on two independent carboradical parameters consistently support the rate-limiting benzylic radical formation for the dioxoruthenium(VI)-mediated styrene epoxidation.

In accord with the Hammond postulate, the alkene epoxidation by the milder oxidant  $[Ru^{VI}(TMOPP)O_2]$  (**1c**) proceeds via a more product-like transition state. In contrast, alkene oxidation by the more reactive oxidants **1a** and **1b** has led to a more reactant-like transition state. For a more product-like transition state, i.e., more carboradical-like, the rate of the alkene epoxidation by  $[Ru^{VI}(TMOPP)O_2]$  was found to be more sensitive to the para-substituent effect manifested by a larger magnitude of its  $\rho_{JJ^*}$ ,  $\rho_{mb}$  (Jiang and Ji) and  $\rho_{TE^*}$  (Wu) values.

**Proposed Mechanism.** We can conclude that the oxidation of aromatic alkenes by dioxoruthenium(VI) porphyrins involves the rate-limiting formation of a benzylic radical intermediate. The radical intermediate would then partition between ring closure and a C-C rotation/cyclization thereby producing *cis*- and *trans*-epoxides, respectively. The participation of a carboradical intermediate in the oxometal-mediated alkene epoxidations is not without precedent; oxidation systems involving the  $[Mn^{IV}(O)(TMP)]$ ,<sup>44a</sup>  $[Fe^{IV}(O)(TMP)]$  ( $H_2TMP =$  tetramesitylporphyrin),<sup>44b</sup>  $[Mn^V(O)(salen)(X)]$ ,<sup>32</sup> and  $[Ru^{IV}(O)(L^1)(L^2)]^{2+}$  ( $L^1$  and  $L^2 =$  polypyridine ligands)<sup>7e</sup> complexes have already been proposed to proceed via a radical intermediate.

Apparently, the stereoretention of the *cis*-alkene oxidations can be influenced by nearby bulky substituents. For example, the *cis*- $\beta$ -methylstyrene oxidation by  $[Ru^{VI}(TDCPP)O_2]$  and  $[Ru^{VI}(TMOPP)O_2]$  are highly stereoselective, whereas the reaction with  $[Ru^{VI}(DPP)O_2]$  results a mixture of *cis*- and *trans*-epoxides. Presumably, the bulky groups tends to hinder the C-C rotation of the benzylic radical intermediate, resulting in a high degree of stereoretention for the *cis*-alkene oxidations. Benzal-

dehyde, the C=C bond cleavage product, should result from the reaction of the carboradical species with dissolved dioxygen.<sup>44</sup>

## Conclusion

With regard to the mechanism of alkene epoxidation by bulky dioxoruthenium(VI) porphyrins, the following findings are summarized:

(1) The stereoselectivity for the epoxide formation varies with alkenes in the order of *cis*-stilbene > *cis*- $\beta$ -methylstyrene > *cis*- $\beta$ -deuteriostyrene, whereas the sterically bulky dioxoruthenium(VI) porphyrins such as  $[Ru^{VI}(TDCPP)O_2]$  and  $[Ru^{VI}(TMOPP)O_2]$  can afford a better stereoretention than  $[Ru^{VI}(DPP)O_2]$ .

(2) The observation of inverse secondary KIE for the oxidation of  $\beta$ -*d*<sub>2</sub>-styrene [ $k_H/k_D = 0.87$  for **1a**, 0.86 for **1b**] and its absence in the  $\alpha$ -deuteriostyrene oxidations discounts strongly a rate-limiting formation of a metal-oxetane and a concerted oxene insertion mechanism.

(3) For the oxidation of para-substituted styrenes, a linear dual-parameter Hammett correlation was established using  $\sigma_{mb}$  and  $\sigma_{JJ^*}$  parameters, which is consistent with the rate-limiting formation of a benzylic radical intermediate. The  $|\rho_{JJ^*}/\rho_{mb}| > 1$  suggests that the generation of the carboradical intermediate is controlled principally by spin delocalization effect.

The sterically encumbered  $[Ru^{VI}(TDCPP)O_2]$  and  $[Ru^{VI}(TMOPP)O_2]$  readily oxidize *trans*- $\beta$ -methylstyrene in good yields. The comparable  $\Delta S^\ddagger$  values for the *trans*- $\beta$ -methylstyrene and styrene oxidations by  $[Ru^{VI}(TDCPP)O_2]$  and  $[Ru^{VI}(TMOPP)O_2]$  suggest a similar degree of oxidant-alkene association in the transition state. Because a side-on approach of *trans*-alkene is not favored by the bulky substituents, a head-on approach model is postulated.

## Experimental Section

All solvents were purified by the standard procedures before use. Benzaldehyde, 2,6-dichlorobenzaldehyde, 2,4,6-trimethoxybenzaldehyde, and pyrrole were either distilled or purified by the standard methods prior to use. Bromine, *m*-chloroperoxybenzoic acid (Merck), dodecacarbonyltriruthenium(0), and pyrazole (Aldrich) were used as received. 2,3,5,7,10,12,13,15-,18,20-Dodecaphenylporphyrin ( $H_2DPP$ ) was prepared using the previously reported procedure.<sup>18d</sup> *meso*-Tetrakis(2,6-dichlorophenyl)porphyrin ( $H_2TDCPP$ ) and *meso*-tetrakis(2,4,6-trimethoxyphenyl)porphyrin ( $H_2TMOPP$ ) were synthesized according to Lindsey's method.<sup>45</sup> The alkene substrates were purified by either vacuum distillation or recrystallization, and their purities were checked by GC or <sup>1</sup>H NMR analysis. *cis*- $\beta$ -Methylstyrene,<sup>46</sup> *cis*- $\beta$ -deuteriostyrene,<sup>46</sup>  $\beta$ -*d*<sub>2</sub>-styrene,<sup>47a,b</sup> and  $\alpha$ -deuteriostyrene<sup>47a,c</sup> were prepared according to the literature procedures. The preparation and characterization of  $[Ru^{VI}(DPP)O_2]$  and  $[Ru^{IV}(DPP)(pz)_2]$  have been reported elsewhere.<sup>18d</sup>

**$[Ru^{II}(\text{Por})(\text{CO})(\text{py})]$ ,  $H_2\text{Por} = H_2TDCPP$  and  $H_2TMOPP$ .**  
A mixture of  $Ru_3(\text{CO})_{12}$  (200 mg, 0.313 mmol) and free base porphyrin ( $H_2\text{Por}$ ) was heated in molten naphthalene (220 °C)

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under an argon atmosphere for 24 h. After cooling to room temperature, the mixture was dissolved in toluene, and the solution was loaded directly onto an alumina column. Naphthalene, unreacted  $\text{Ru}_3(\text{CO})_{12}$ , and  $\text{H}_2\text{Por}$  were eluted by toluene. The desired ruthenium porphyrin complex was collected using a chloroform/ethyl acetate mixture (95:5 v/v for  $\text{H}_2\text{Por} = \text{H}_2\text{TDCPP}$ ) or chloroform/methylene chloride mixture (1:1 v/v for  $\text{H}_2\text{Por} = \text{H}_2\text{TMOPP}$ ) as the eluant. Upon addition of methanol (ca. 20 mL), the solution was concentrated until the  $[\text{Ru}^{\text{II}}(\text{Por})(\text{CO})(\text{MeOH})]$  complex started to precipitate as a red solid. Recrystallization of the  $[\text{Ru}^{\text{II}}(\text{Por})(\text{CO})(\text{MeOH})]$  complex in a pyridine/dichloromethane/benzene solution [6:3:1 (v/v), 10 mL] afforded the titled complex as a dark purple crystal.

Yield for  $[\text{Ru}^{\text{II}}(\text{TDCPP})(\text{CO})(\text{py})]$ : 90% based on  $\text{H}_2\text{TDCPP}$ . IR(KBr): 1947  $\text{cm}^{-1}$  ( $\nu_{\text{C}=\text{O}}$ ). UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}/\text{nm}$  (log  $\epsilon$ ): 410 (5.14), 530 (4.23), 558 (sh) (3.59).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  7.73 (m, 12H), 8.44 (s, 8H). FAB-MS:  $m/z$  1023 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{46}\text{H}_{24}\text{Cl}_8\text{N}_4\text{O}_2\text{Ru}$ : C, 53.06; H, 2.46; N, 5.27. Found: C, 53.27; H, 2.60; N, 5.10.

Yield for  $[\text{Ru}^{\text{II}}(\text{TMOPP})(\text{CO})(\text{py})]$ : 80% based on  $\text{H}_2\text{TMOPP}$ . IR(KBr): 1938  $\text{cm}^{-1}$  ( $\nu_{\text{C}=\text{O}}$ ). UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}/\text{nm}$  (log  $\epsilon$ ): 412 (5.46), 528 (4.40), 560 (sh) (3.40).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  3.55 (s, 12H), 3.67 (s, 12H), 4.10 (s, 12H), 6.61 (m, 8H), 8.57 (s, 8H). FAB-MS:  $m/z$  1131 ( $\text{M}^+ + 1$ ). Anal. Calcd for  $\text{C}_{58}\text{H}_{56}\text{N}_4\text{O}_{14}\text{Ru}$ : C, 61.42; H, 4.94; N, 4.94. Found: C, 60.21; H, 5.03; N, 4.87.

**$[\text{Ru}^{\text{VI}}(\text{Por})\text{O}_2]$ ,  $\text{H}_2\text{Por} = \text{H}_2\text{TDCPP}$  (**1b**) and  $\text{H}_2\text{TMOPP}$  (**1c**).** A methylene chloride solution (20 mL) of  $[\text{Ru}^{\text{II}}(\text{Por})(\text{CO})(\text{MeOH})]$  (40  $\mu\text{mol}$ ) was treated with *m*-chloroperoxybenzoic acid (100 mg, 58  $\mu\text{mol}$ ). The mixture was stirred for 5 min, and the resultant brown solution was loaded onto an alumina column. The product ruthenium complex was then eluted with methylene chloride (ca. 20 mL). Addition of purified *n*-hexanes induced precipitation of the complex as a purple microcrystalline solid. The solid was then collected on a frit, washed with anhydrous methanol, and then dried in vacuo.

Yield for **1b**: 80%. IR (KBr): 825  $\text{cm}^{-1}$  ( $\nu_{\text{RuO}_2}$ ), 1019  $\text{cm}^{-1}$  (oxidation state marker band). UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}/\text{nm}$  (log  $\epsilon$ ): 420 (5.42), 521 (4.36), 572 (3.86).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  7.81 (m, 12H), 8.89 (s, 8H). FAB-MS:  $m/z$  1012 ( $\text{M}^+$ ), 989 ( $\text{M}^+ - 2\text{O}$ ). Anal. Calcd for  $\text{C}_{44}\text{H}_{20}\text{Cl}_2\text{N}_4\text{O}_2\text{Ru}$ : C, 51.71; H, 1.97; N, 5.49. Found: C, 51.80; H, 2.20; N, 5.17.

Yield for **1c**: 75%. IR (KBr): 820  $\text{cm}^{-1}$  ( $\nu_{\text{RuO}_2}$ ), 1018  $\text{cm}^{-1}$  (oxidation state marker band). UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}/\text{nm}$  (log  $\epsilon$ ): 424 (5.42), 521 (4.36), 563 (3.86).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  3.61 (s, 24H), 4.12 (s, 12H), 6.66 (s, 8H), 8.97 (s, 8H). FAB-MS:  $m/z$  1132 ( $\text{M}^+ + 1$ ), 1101 ( $\text{M}^+ - 2\text{O}$ ). Anal. Calcd for  $\text{C}_{56}\text{H}_{52}\text{N}_4\text{O}_{14}\text{Ru}$ : C, 60.80; H, 4.74; N, 5.07. Found: C, 61.11; H, 4.36; N, 4.89.

**Stoichiometric Oxidation of Alkenes by Dioxoruthenium(VI) Porphyrins.** To a degassed methylene chloride solution (5 mL) containing pyrazole (2% w/w) and alkenes (2 mmol) was added  $[\text{Ru}^{\text{VI}}(\text{Por})\text{O}_2]$  (30  $\mu\text{mol}$ ) under an argon atmosphere. After stirring for 12 h, the reaction mixture was filtered through a short alumina column with hexanes/ethyl acetate (9:1) as the eluant to remove the ruthenium complex.

The organic products were then analyzed and quantified, after addition of an internal standard, by either gas chromatography or  $^1\text{H}$  NMR spectroscopy.

The product ruthenium(IV) porphyrin was eluted by methylene chloride, and addition of acetonitrile led to the isolation of  $[\text{Ru}^{\text{IV}}(\text{Por})(\text{pz})_2]$  ( $\text{H}_2\text{Por} = \text{H}_2\text{DPP}$  (**2a**),  $\text{H}_2\text{TDCPP}$  (**2b**), and  $\text{TMOPP}$  (**2c**)) as a dark purple solid. Yield: 70–80%. For the characterization data of  $[\text{Ru}^{\text{IV}}(\text{DPP})(\text{pz})_2]$ , see ref 6k.

**$[\text{Ru}^{\text{IV}}(\text{TDCPP})(\text{pz})_2]$  (**2b**).** Yield: 75%. UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}/\text{nm}$  (log  $\epsilon$ ): 401 (5.19), 520 (4.01). IR (KBr): 1006  $\text{cm}^{-1}$  (oxidation state marker band). FAB-MS:  $m/z$  1123 ( $\text{M}^+$ ), 989 ( $\text{M}^+ - 2\text{pz}$ ). Anal. Calcd for  $\text{C}_{50}\text{H}_{32}\text{Cl}_8\text{N}_8\text{Ru}$ : C, 53.42; H, 2.32; N, 9.97. Found: C, 53.20; H, 2.62; N, 9.68.  $\mu_{\text{eff}}$  (Evan's method) = 2.68  $\mu_{\text{B}}$  ( $\text{CHCl}_3$ , room temperature).

**$[\text{Ru}^{\text{IV}}(\text{TMOPP})(\text{pz})_2]$  (**2c**).** Yield: 65%. UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}/\text{nm}$  (log  $\epsilon$ ): 406 (5.06), 521 (3.84). IR (KBr): 1004  $\text{cm}^{-1}$  (oxidation state marker band). FAB-MS:  $m/z$  1207 ( $\text{M}^+$ ), 1140 ( $\text{M}^+ - \text{pz}$ ), 1074 ( $\text{M}^+ + 1 - 2\text{pz}$ ). Anal. Calcd for  $\text{C}_{62}\text{H}_{58}\text{N}_8\text{O}_{12}\text{Ru}$ : C, 61.64; H, 4.81; N, 9.28. Found: C, 61.41; H, 4.96; N, 9.09.  $\mu_{\text{eff}}$  (Evan's method) = 2.88  $\mu_{\text{B}}$  ( $\text{CHCl}_3$ , room temperature).

**Kinetic Measurements for Alkene Epoxidations by Dioxoruthenium(VI) Porphyrins.** Kinetic experiments were performed on a Hewlett-Packard HP8452A UV-vis diode array spectrophotometer interfaced with an IBM-compatible PC. The measurements were made in a standard 1.0 cm quartz cuvettes. The temperature of the solution was maintained to within  $\pm 0.2$  °C during the kinetic studies with the use of a Lauda RM6 circulating water bath. The oxidation of alkenes by  $[\text{Ru}^{\text{VI}}(\text{Por})\text{O}_2]$  was followed by monitoring the decrease of the Soret absorption band under the condition that the alkene concentration was at least 100-fold in excess of  $[\text{Ru}^{\text{VI}}(\text{Por})\text{O}_2]$ . The pseudo-first-order rate constants,  $k_{\text{obs}}$ , were obtained by nonlinear least-squares fits of  $(A_f - A_t)$  to time  $t$  according to the equation

$$(A_f - A_t) = (A_f - A_i) \exp(-k_{\text{obs}} t)$$

where  $A_i$  and  $A_f$  are the initial and final absorbances, respectively, and  $A_t$  is the absorbance at time  $t$ . Kinetic data over four half-lives ( $t_{1/2}$ ) were used for the fitting. The second-order rate constants,  $k_2$ , were evaluated from the linear fit of the  $k_{\text{obs}}$  values to the alkene concentrations.

The activation enthalpies ( $\Delta H^\ddagger$ ) and entropies ( $\Delta S^\ddagger$ ) were calculated from the linear plot of  $\ln(k_2/T)$  versus  $(1/T)$  according to the Eyring equation:

$$\ln(k_2/T) = \ln(R/N_A \hbar) + \Delta S^\ddagger/R - \Delta H^\ddagger/RT$$

where  $T$  is the temperature (K),  $N_A$  is Avogadro's number,  $R$  is the universal gas constant, and  $\hbar$  is Planck's constant.

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