

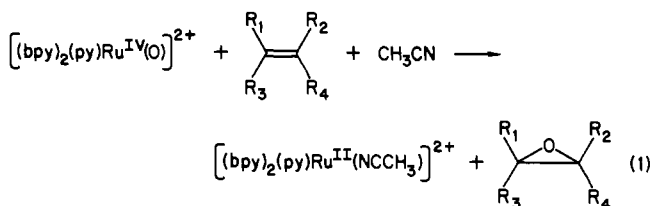
Communications

Epoxidation and Catalytic Oxidation of Olefins Based on a Ru^{IV}=O/Ru^{II}-OH₂ Couple

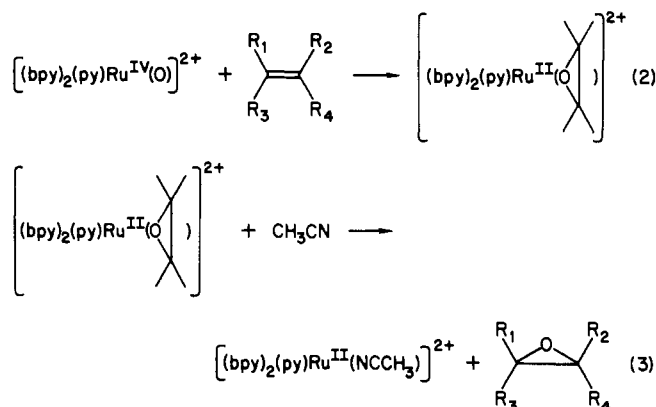
Sir:

Metal oxo intermediates have been invoked as the reactive entities in metalloporphyrin-catalyzed epoxidations.¹ The ruthenium(IV) oxo complexes [(bpy)₂(py)Ru(O)](ClO₄)₂ and [(trpy)(bpy)Ru(O)](ClO₄)₂ (bpy = 2,2'-bipyridine; py = pyridine; trpy = 2,2',2''-terpyridine) have proven to be useful stoichiometric and/or electrocatalytic oxidants for a variety of organic functional groups.² Balavoine and co-workers have recently reported the stereospecific epoxidation of olefins catalyzed by ruthenium complexes in the presence of NaIO₄ as oxidant and speculate that the active catalyst is a ruthenium oxo intermediate.³ We report here that the reactivity of the polypyridyl-based ruthenium(IV) oxo complexes extends to olefins where in acetonitrile clean, well-defined epoxidation occurs by reactions whose mechanisms can be defined in some detail.

Addition of styrene, norbornylene, or stilbene to acetonitrile solutions containing [(bpy)₂(py)Ru(O)]²⁺ leads to the quantitative appearance of [(bpy)₂(py)Ru(NCCH₃)]²⁺ (λ_{max} = 440 nm, ε = 8000 M⁻¹ cm⁻¹), as shown in Figure 1. Analysis by ¹H NMR shows the appearance of the corresponding epoxide in solution, and spectrophotometric titrations show that the reaction stoichiometry is as given in eq 1. The results of kinetics studies in



acetonitrile are summarized in Table I. All three reactions are first order in both [(bpy)₂(py)Ru(O)]²⁺ and olefin. From the rate law and product studies, the mechanism of epoxidation may involve a simple O atom insertion into the olefin followed by solvolysis of bound epoxide as shown in eq 2 and 3, as found earlier, for



example, for the oxidation of PPh₃ to OPPh₃.⁴ The Ru^{IV}=O complexes have a propensity to undergo 2-electron changes, and the redox step may involve a concerted 2-electron, O atom transfer. However, the appearance of 5% isomerization in the epoxidation of *cis*-stilbene is a notable observation, and we cannot rule out more complex mechanisms such as the formation of metallo-cyclooxetane intermediates as initially proposed by Sharpless.⁵ In its reactions, Ru^{IV}=O may differ considerably from the more strongly oxidizing Mn- and Fe-porphyrin-based oxidants described previously where the initial redox step may be largely 1-electron in character.¹

The oxidation of olefins by [(bpy)₂(py)Ru(O)]²⁺ or [(trpy)(bpy)Ru(O)]²⁺ can be made catalytic with OCl⁻ as oxidant by using the phase-transfer conditions described earlier for other systems.¹ In aqueous solution OCl⁻ oxidizes the aqua complexes to Ru^{IV}=O, as shown by spectrophotometric titrations and isolation of the oxo complexes as ClO₄⁻ salts following the addition of NaClO₄. In a typical catalytic experiment, 0.02 mmol of either [(bpy)₂(py)Ru(OH₂)]²⁺ or [(trpy)(bpy)Ru(OH₂)]²⁺ was dissolved in 10 mL of CH₂Cl₂ with a 100-fold excess of olefin and 0.04 mmol of the phase-transfer catalyst benzyldimethyltetradecylammonium chloride. Ten milliliters of a NaOCl solution (chlorine 5% minimum, Aldrich Chemical Co.) and 10 mL of a HPO₄²⁻/PO₄³⁻ phosphate buffer solution (pH 10.5) were layered over the CH₂Cl₂.⁶ The reaction mixture was stirred vigorously for 3 h, with aliquots of the organic layer monitored by gas chromatography every 30 min. After 3 h, the organic layer was extracted with ether to precipitate the metal complex. Ether and CH₂Cl₂ were removed under reduced pressure, and the remaining liquid was analyzed for epoxide and benzaldehyde by ¹H NMR and gas

- As examples, note: (a) Tabushi, I.; Kodera, M.; Yokoyama, M. *J. Am. Chem. Soc.* **1985**, *107*, 4466. (b) Meunier, B.; Guilmet, E.; DeCarvalho, M.; Poilblanc, R. *J. Am. Chem. Soc.* **1984**, *106*, 6668. (c) Collman, J. P.; Kodadek, T.; Raybuck, S. A.; Braumann, J. I.; Meunier, B.; Hayashi, T. *J. Am. Chem. Soc.* **1985**, *107*, 2000. (d) Groves, J. T.; Nemo, T. E. *J. Am. Chem. Soc.* **1983**, *105*, 5786. (e) VanAtta, R. B.; Franklin, C. C.; Valentine, J. S. *Inorg. Chem.* **1984**, *23*, 4123.
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(6) It is necessary to control pH when the polypyridine-based oxidants are used because in basic solutions (pH > 12) relatively rapid oxidation of the ligands occurs: Roecker, L.; Kutner, W.; Gilbert, J. C.; Simmons, M.; Murray, R. W.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 3784.

Table I. Kinetics Data for the Epoxidation of Olefins by $[(bpy)_2(py)Ru(O)]^{2+}$ in Acetonitrile at Room Temperature

substrate	product(s)	$k(25\text{ }^\circ\text{C})$, $M^{-1}\text{ s}^{-1}$	ΔH^\ddagger , kcal mol^{-1}	ΔS^\ddagger , eu
styrene	styrene oxide	1.48×10^{-2}	7.2 ± 2.3	-43 ± 7
<i>trans</i> -stilbene	<i>trans</i> -stilbene oxide	1.09×10^{-2}		
<i>cis</i> -stilbene	<i>cis</i> -stilbene oxide (95%) ^a <i>trans</i> -stilbene oxide (5%)	1.43×10^{-3}		

^a Yields based on $^1\text{H NMR}$.

Table II. Catalytic Oxidation of Olefins by $[(trpy)(bpy)Ru(OH_2)]^{2+}/\text{NaOCl}$ at pH 10.5^a

olefin	% conversion	products	
		\triangle	PhCHO
styrene	60	22	78
<i>trans</i> -stilbene	58	11	71
<i>cis</i> -stilbene	35	trace	99

^a Conditions as described in text; reaction time of 3 h.

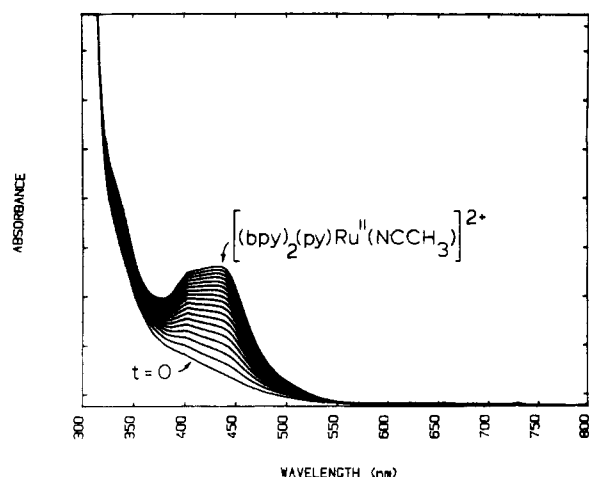
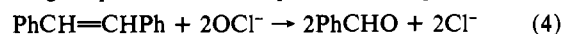


Figure 1. Spectral changes with time in the oxidation of styrene ($5 \times 10^{-2}\text{ M}$) by $[(bpy)_2(py)Ru(O)]^{2+}$ ($5 \times 10^{-5}\text{ M}$). Spectra were recorded at 1-min intervals. The initial spectrum after mixing is labeled $t = 0$, and the spectrum after 17 min, labeled $[(bpy)_2(py)Ru(NCCH_3)]^{2+}$, has λ_{max} at 440 nm ($\epsilon = 8000\text{ M}^{-1}\text{ cm}^{-1}$).

chromatography. The results of the $^1\text{H NMR}$ analysis are summarized in Table II. In blank experiments without added catalyst only trace amounts of oxidized products appeared. Blank experiments also showed that styrene oxide is stable toward further oxidation under our reaction conditions with or without added catalyst. A high percentage of PhCHO as a product of the NaOCl-catalyzed oxidation of styrene has been found under similar conditions based on RuO_4 or $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$,⁷ and more recently, Eskenazi et al. have reported that the selectivity of epoxidation based on the $\text{RuCl}_3 \cdot n\text{H}_2\text{O}/\text{NaIO}_4$ system can be controlled by the addition of substituted bipyridines or phenanthrolines.⁸ We cannot yet account for the change in product distribution and the appearance of PhCHO under catalytic conditions. Even though OCl^- oxidation of the aqua complexes leads to $\text{Ru}^{\text{IV}}=\text{O}$ in water, the actual state of the catalyst in the catalytic runs is unknown.

Although simple, quantitative epoxidation is clearly an accessible pathway in dry acetonitrile, it seems clear from observations made here and earlier that there is an extensive chemistry of olefin oxidation by $\text{Ru}^{\text{IV}}=\text{O}$: (1) electrocatalytic oxidation of *trans*- $\text{CH}_3\text{CH}=\text{CHOO}_2^-$ in water occurs at the allylic position to give the corresponding diacid,^{2a} (2) under catalytic conditions

in the hypochlorite oxidations a pathway leading to oxidative olefin bond cleavage, eq 4, occurs in competition with epoxidation or,



perhaps, by further oxidation of bound epoxide, and (3) in reactions currently under investigation in acetonitrile, olefins containing $\alpha\text{-C-H}$ bonds, e.g., cyclohexene or 2,3-dimethyl-2-butene, undergo allylic oxidation preferentially over epoxidation.

Acknowledgments are made to the National Science Foundation and the National Institutes of Health for support of this research.

Registry No. $[(bpy)_2(py)Ru(O)]^{2+}$, 67202-43-1; $[(bpy)_2(py)Ru(OH_2)]^{2+}$, 70702-30-6; $[(trpy)(bpy)Ru(OH_2)]^{2+}$, 20154-63-6; NaOCl, 7681-52-9; styrene, 100-42-5; *trans*-stilbene, 103-30-0; *cis*-stilbene, 645-49-8.

Department of Chemistry
The University of North Carolina
Chapel Hill, North Carolina 27514

John C. Dobson
Won K. Seok
Thomas J. Meyer*

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Reduction of Dirhodium(II) Complexes of the Type $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_3(\text{L})]^+$. An ESR Investigation

Sir:

The electrooxidation of dirhodium complexes of the forms $\text{Rh}_2(\text{O}_2\text{CR})_4^{1-7}$ and $\text{Rh}_2(\text{O}_2\text{CCH}_3)_n(\text{RNOCR}')_{4-n}^{8-13}$ where RNOCR' is the anion of acetamide or acetanilide has been a subject of numerous publications. However, very few studies have reported electroreductions for these type complexes. The scarcity of such studies is due to the fact that the electroreductions of all $\text{Rh}_2(\text{O}_2\text{CR})_4$ complexes are irreversible⁷ while $\text{Rh}_2(\text{O}_2\text{CCH}_3)_n(\text{RNOCR}')_{4-n}$ complexes show no reduction waves within the range of investigated electrochemical solvents.

Until recently, reversible reductions had not been reported for any dirhodium complexes, nor was there any spectral characterization of the chemical or electrochemical reduction products.

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