

# Reconsidered mechanism in Ru<sup>III</sup>(hedta)-catalyzed epoxidation of stilbenes

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## Abstract

The *cis*-stilbene oxide/*trans*-stilbene oxide isomer assignment given formerly in *Inorg. Chim. Acta*, 193 (1992) 217 should be reversed. This assignment was based on the <sup>1</sup>H NMR spectra of the stilbene oxides given in *The Varian High Resolution NMR Spectral Catalog*, Vol. 2, which is in error. The large amount of *trans*-oxide versus *cis*-oxide (5.5:1) from the *cis*-stilbene epoxidation by [Ru<sup>III</sup>(hedta)]/t-BuOOH, and 100% *trans*-oxide from *trans*-stilbene, is reinterpreted as indicative of a radicaloid intermediate in ≥ 85% of the reaction channels. Comparisons are made with 15 ruthenium oxo catalysts which epoxidize stilbenes. Two categories are observed which are (A) stereoretentive Ru<sup>IV</sup>O catalysts or sterically hindered Ru<sup>V</sup>O porphyrin oxidants, and (B) those which give isomer mixtures for *Z*-olefins and which are less hindered Ru<sup>V</sup>O and Ru<sup>VI</sup>O catalysts. The mechanistic aspects of these epoxidations are discussed.

## Introduction

In a recent paper in this journal we reported on the [Ru<sup>III</sup>(hedta)]-catalyzed epoxidation of stilbenes using tert-butylhydroperoxide (t-BuOOH) as the oxygen source [1]. We incorrectly reversed the assignment of the stereochemistries of the *cis*-stilbene oxide and *trans*-stilbene oxide products. This regrettable error was made because we assigned the products according to the reaction product <sup>1</sup>H NMR spectra as specified for these compounds in two well-accepted reference works (*CRC Handbook of Data on Organic Compounds*, 2nd edn. [2] and the *Varian High Resolution NMR Spectra Catalog*, Vol. 2 [3]). It has come to our attention in the course of preparation of a review article by this author that the isomer assignments given in refs. 2 and 3 are opposed to the <sup>1</sup>H NMR spectrum for *trans*-stilbene in the Aldrich NMR Spectral Library [4]. A search of the literature has shown that there has been some confusion as to the validity of the isomer assignment for stilbene oxides. The correct assignments should be  $H_a = 3.88$  ppm,  $H_b$  (phenyl rings) = 7.39 ppm for the *trans*-stilbene oxide and  $H_a = 4.36$  ppm,  $H_b = 7.20$  ppm for the *cis*-stilbene oxide, the reverse of the basis of our assignment [2, 3]. This means that the headings of the entries for stilbene oxide product yields should be reversed in Tables 1, 2 and 3 of the former text [1]. The percentage yields reported are correct for the opposite isomer as stated in the former text. This feature necessitates a reconsideration of the mechanisms of

stilbene epoxidation and the relative proportion of the reactivity which we attributed to the concerted O-atom transfer pathway (preserving stereochemistry) and that of acyclic pathways of electron transfer or carbonium ion character that provide for inversion and mixtures of product stereochemistry compared to the reactant *cis*- or *trans*-stilbene [5–11].

Based on the former incorrectly assigned product yields, we had concluded that the dominant chemical pathway was a concerted O-atom transfer with electron transfer and acyclic carbonium ion routes relegated to a lesser role for *cis*-stilbene. *Trans*-stilbene was assigned a high reactivity involving stepwise outer-sphere electron transfer followed by radical capture, rotation within the acyclic radical, and closure to prepare the *cis*-oxide. With the correct isomer product assignment the proper interpretation is that of electron transfer followed by trapping of a radicaloid intermediate as the main pathway for both *cis*-stilbene and *trans*-stilbene. In this way *trans*-stilbene is epoxidized with retention as the *trans*-oxide because the *trans* form of the radical suffers less strain than a *cis*-stilbene radical intermediate. Rotation within the trapped acyclic radical derived from *cis*-stilbene provides a fraction of *cis*-oxide depending on the rate of rotation within the radicaloid intermediate and ring closure to complete epoxide formation [12, 13].

With this revision in our assessment of the mechanism the [Ru<sup>III</sup>(hedta)]/t-BuOOH epoxidation process for

stilbenes, the chemical behavior of the  $[\text{Ru}^{\text{V}}(\text{O}^{2-})(\text{hedta})] \leftrightarrow [\text{Ru}^{\text{III}}(\text{O})(\text{hedta})]$  intermediate is consistent with a pattern which can be perceived from divergent types of Ru-oxo catalysts including Ru(porphyrins) [13–16], Ru(diphos)<sub>2</sub>Cl [12], Ru(tetramethylcyclam) [17], Ru(bipyridine)<sub>2</sub> [18–20], Ru(py)<sub>2</sub>(O<sub>2</sub>CR)<sub>2</sub> [21], Ru(salen) [22], Ru(pyridylamines) [23] and Ru(pac) (pac = polyaminopolycarboxylate ligands) [1, 24, 25] systems. In this paper, we discuss these trends after discussing the mechanistic implications for the  $[\text{Ru}^{\text{III}}(\text{hedta})]$ -catalyzed epoxidation upon proper assignment of the *cis*-stilbene oxide and *trans*-stilbene oxide product amounts from the former text [1].

## Experimental

The methods of data collection, sample preparation, analysis, and reagent sources are those specified in the former paper [1]. Reaction times for the epoxidation of stilbenes were 4.0 h, followed by extraction of stilbene oxides and unreacted stilbenes in CDCl<sub>3</sub>. <sup>1</sup>H and <sup>13</sup>C NMR spectra for the identification of organic reactants and products were obtained on Bruker AF 300 and Bruker AF 500 NMRs. CH<sub>2</sub>Cl<sub>2</sub> served as an internal integration standard.

## Results and discussion

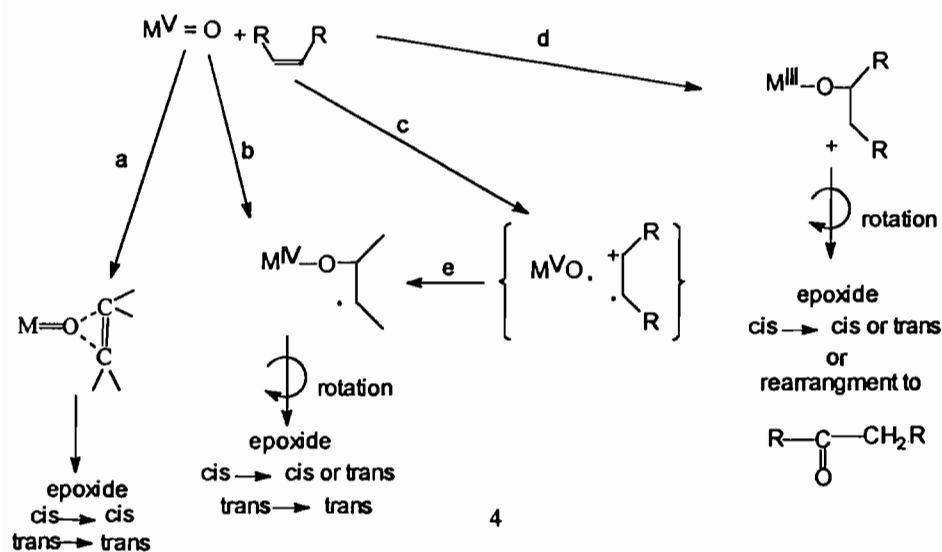
In the former paper it was shown that catalytic activity increases in total  $[\text{Ru}^{\text{III}}(\text{hedta})]$  catalyst concentration up to *c.*  $5.7 \times 10^{-4}$  M and then decreases due to the formation of inactive oxo-bridged complexes. From *cis*-stilbene a maximum yield of 63.5% *trans*-oxide, 11.0% *cis*-oxide and 5.6% benzaldehyde were found at  $5.72 \times 10^{-4}$  M catalyst and initial concentrations of 0.628 M t-BuOOH and saturated *cis*-stilbene ( $3.26 \times 10^{-4}$  mol *cis*-stilbene in contact with 2.15 ml of t-BuOOH solution). On twelve independent runs at various starting amounts of  $[\text{Ru}^{\text{III}}(\text{hedta})]$  catalyst, it was observed that the product ratio of *trans*-oxide:*cis*-oxide is relatively constant at 5.5:1 given here in the correct isomer assignment. Benzaldehyde formation varied from 2.4 to 8.2%, averaging 5.1%. The total mass balance in our methods [1], matched those of Castellino and Bruce [5] with Fe(III) and Mn(III) porphyrins plus iodobenzene and peroxycarboxylic acids and with Hecht and co-workers [11] using Fe<sup>III</sup> and Mn<sup>III</sup> bleomycin reagents plus iodobenzene or peroxide. Our mass balance of 81% recovered materials was nearly the same as Castellino and Bruce (76% [5]). The oxidation of the benzaldehyde product to the water soluble benzoic acid was shown for the  $[\text{Ru}^{\text{III}}(\text{hedta})]/$

t-BuOOH reagent previously [1, 26]. Any benzoic acid would remain unextracted and probably accounts for the major portion of unrecovered materials in our methods.

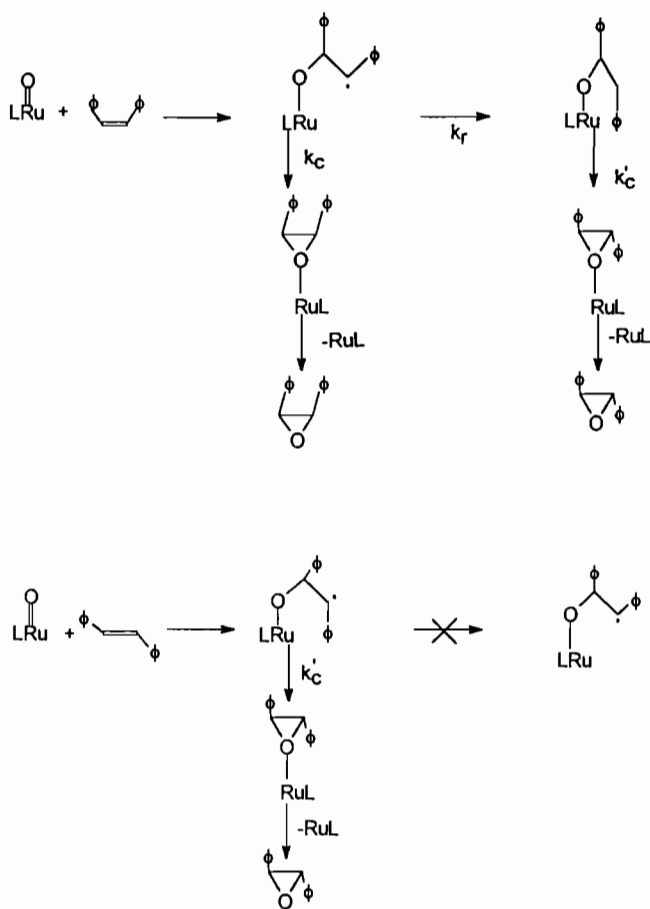
The *trans*-stilbene epoxidation by  $[\text{Ru}^{\text{III}}(\text{hedta})]/$  t-BuOOH was catalyzed by Ru(hedta) (added either in the initial Ru<sup>II</sup> or Ru<sup>III</sup> form) and by  $[\text{Ru}^{\text{II}}(\text{N,N}'\text{-dimethyledda})]$  giving exclusively the *trans*-oxide (no detectable *cis*-oxide) and 1.0 to 6.2% benzaldehyde yields of the *trans*-oxide were 45.6% from  $[\text{Ru}^{\text{II}}(\text{hedta})]^{-}$ , 49.1% from  $[\text{Ru}^{\text{II}}(\text{N,N}'\text{-dimethyledda})]$  and 65.1% from  $[\text{Ru}^{\text{III}}(\text{hedta})]$  [1]. The independence of the *trans*-oxide/*cis*-oxide product distribution from *cis*-stilbene in the presence of Ar, CO or O<sub>2</sub> and the absence of additional benzaldehyde in the presence of O<sub>2</sub>, nor any lesser activity for the  $[\text{Ru}^{\text{III}}(\text{hedta})]/$  t-BuOOH system under CO was discussed previously [1].

### Conclusions on the epoxidation mechanism

The larger amount of *trans*-stilbene oxide compared to *cis*-stilbene oxide from *cis*-stilbene (*c.* 5.5:1) implies that the epoxidation process is dominated by the acyclic pathways involving an aspect of electron transfer to generate a radical ion intermediate. The various pathways of concerted O-atom transfer (route a in Scheme 1), electron transfer/radical capture (pathways c and e), radical addition (pathway b) and the acyclic carbonium route (pathway d) have been described in the reactivity of metalloporphyrin oxo catalysts and metallobleomycin catalysts for the epoxidation of olefins [5–11]. When *E*-olefins (*trans*-stilbene) are epoxidized with retention of stereochemistry and *Z*-olefins (*cis*-stilbene) produce mixtures of *trans*-oxide and *cis*-oxide with a predominance of *trans*-oxide this is evidence of the pathways of radical character as the main channel(s) to products [5, 13, 16]. A radical addition (path b) or outer-sphere electron transfer/radical capture route (path c plus e) or two-electron oxidation/carbonium ion (path d) generates intermediates which allow for rotation of the C–C single bond. Steric repulsions of the phenyl rings favor rotation into the less-strained *trans* arrangement. (Scheme 2). The rotation process (*k<sub>r</sub>*) competes with radical capture (*k<sub>c</sub>*) of the *cis* orientation. Therefore the *cis*-stilbene produces a *trans*-oxide:*cis*-oxide ratio dependent upon the ratio of the first-order rate constants for rotation versus ring closure. The *trans*-isomer on the other hand generates a radical in the less-strained orientation. A rotation toward the *cis* orientation is energetically uphill. The rate of this rotation process cannot compete successfully with the radical capture by ring closure. Evidence for the coordinated epoxide intermediate, prior to release of the epoxide product, has been obtained by <sup>1</sup>H NMR in the case of β-methylstyrene by the reaction of the epoxide with Ru<sup>II</sup>(TMP) (TMP = tetramesitylporphyr-



Scheme 1.



Scheme 2.

inato) [27]. A comparison of the stereochemical behavior of ruthenium chelate catalysts for which data are available is shown in Table 1. There are two categories of reported catalysis: (A) those exhibiting nearly quan-

titative retention of stereochemistry of the reactant stilbene and (B) those exhibiting a mixture of *cis*-oxide and *trans*-oxide from *cis*-stilbene and other *Z*-olefins, and nearly quantitative production of *trans*-oxide from *trans*-stilbene or *E*-olefins. In category A having stereoretention are all the Ru-oxo catalysts which can be described with certainty as  $\text{Ru}^{\text{IV}}=\text{O} \leftrightarrow \text{Ru}^{\text{II}}-\text{O}$  atom complexes such as Meyer's  $[\text{RuO}(\text{bpy})_2(\text{py})]^{2+}$  complex [18] and sterically controlled  $\text{Ru}^{\text{VI}}\text{O}$  porphyrin catalysts. The other  $\text{Ru}^{\text{VO}}$  and  $\text{Ru}^{\text{VI}}\text{O}$  species almost always are in category B. The severely hindered  $\text{Ru}^{\text{VI}}=\text{O}$  complexes,  $[\text{Ru}(\text{O})_2(\text{TMP})]$  or  $[\text{Ru}(\text{TPP})(\text{O})_2]$  [15, 16, 20], wherein a very crowded binding pocket can strictly retard the rotation of the generated radical from the radicaloid pathways. In such a situation of hindered rotation of the radical the rate ( $k_r$ ) becomes too low to compete with radical capture ( $k_c$ ). In this manner stereochemistry will be preserved by the steric control in the  $\text{Ru}^{\text{VI}}=\text{O}$  binding pocket of  $[\text{Ru}(\text{O})_2(\text{TMP})]$ . This is not a general feature of exposed Ru(porphyrins) as shown by  $[\text{Ru}(\text{OEP})(\text{O})_2]$  [13]. The behavior of  $[\text{Ru}(\text{OEP})(\text{O})_2]$  is similar to  $[\text{Ru}^{\text{III}}(\text{hedta})]/t\text{-BuOOH}$  and other oxidants of group B such as  $[\text{Ru}(\text{diphos})_2\text{Cl}]^+/\phi\text{IO}$  [12].

The origin of these two groups would appear to be the higher formal oxidation state of unhindered  $\text{Ru}^{\text{VO}}$  and  $\text{Ru}^{\text{VI}}\text{O}$  catalysts which are stronger oxidants. These  $\text{Ru}^{\text{VO}}$  and  $\text{Ru}^{\text{VI}}\text{O}$  catalysts belong to group B forming radical intermediates in which radical rotation to a *transoid* arrangement competes with ring closure forming the epoxide.

The  $\text{Ru}^{\text{VO}}$  and  $\text{Ru}^{\text{VI}}\text{O}$  catalysts are stronger oxidants and should form olefin radicals at longer distances by electron transfer, and more readily, since these have a greater redox driving force. This will favor electron

TABLE 1. Ruthenium-oxo stilbene epoxidation catalysts

Catalyst system	Assigned category	Yield (%)						Reference
		From <i>cis</i> -stilbene			From <i>trans</i> -stilbene			
		<i>trans</i> -oxide	<i>cis</i> -oxide	$\phi$ CHO	<i>trans</i> -oxide	<i>cis</i> -oxide	$\phi$ CHO	
[Ru <sup>III</sup> (hedta)]/t-BuOOH	B	49.5–63.5 <sup>a</sup>	10.6–11.0 <sup>a</sup>	~5.5 <sup>a</sup>	45.6–65.1 <sup>a</sup>	0	~5 <sup>a</sup>	this work, 1
[Ru <sup>II</sup> (Me <sub>6</sub> edda)]/t-BuOOH	B	53.2	4.0	7.8	49.1	0	1	1
[Ru <sup>VI</sup> (OEP)(O) <sub>2</sub> ]	B	44	16	7	22	0	6	13
[Ru(diphos) <sub>2</sub> Cl] <sup>+</sup> /φIO; (Ru <sup>VI</sup> ?)	B	21	14	NR <sup>c</sup>	20	0	NR	12
[Ru <sup>VI</sup> (N <sub>2</sub> py) <sub>2</sub> (O) <sub>2</sub> ]	B	18	0	11	27	0	20	23
[Ru <sup>VI</sup> (O) <sub>2</sub> (py) <sub>2</sub> (φCO <sub>2</sub> ) <sub>2</sub> ]	B	50 <sup>b</sup>	50 <sup>b</sup>	NR	100	0	NR	21
[Ru <sup>III</sup> (salen)]/φIO	B	2.4	9	30	12	0	35	22
[Ru <sup>VI</sup> (5,5'-Me <sub>2</sub> bpy) <sub>2</sub> (O) <sub>2</sub> ]	B	15	62	23	55	0	33	19
[Ru(bpy) <sub>2</sub> (py)(OH <sub>2</sub> )]/OCl <sup>-</sup> ; (Ru <sup>IV</sup> )	A	0	trace	99	11	0	77	18
[Ru(bpy) <sub>2</sub> Cl(O)]/IO <sub>4</sub> <sup>-</sup> ; (Ru <sup>VI</sup> ?)	A	0	100	NR	90	0	NR	20
[Ru <sup>VI</sup> (TMP)(O) <sub>2</sub> ]	A	1.5	32.7	NR	16.2	0.1	NR	14
[Ru(TMP)]/pyNO	A	0	98	NR	7	0	NR	15
[Ru <sup>VI</sup> (TPP)(O) <sub>2</sub> ]	A	0	100	NR	45	0	NR	16
[Ru <sup>IV</sup> O(edta)] <sup>2-</sup>	A	NR	NR	NR	100	0	NR	25
[Ru <sup>V</sup> O(edta)] <sup>-</sup>	A	0	39	NR	36	0	NR	24

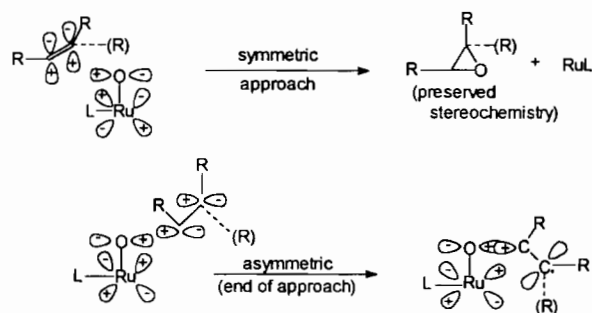
<sup>a</sup>Varies with total Ru<sup>III</sup> catalyst. <sup>b</sup>β-Methylstyrene as substrate. <sup>c</sup>NR = not reported.

transfer pathways for these reagents compared to the weaker Ru<sup>IV</sup>O oxidants. Additionally, the Ru<sup>IV</sup>O bond is longer and weaker than Ru<sup>VI</sup>O bonds as shown by data of Leung and Che concerning the X-ray structures of various tetramethylcyclams, [Ru(O)<sub>2</sub>(14-TMC)]<sup>2+</sup> and [Ru(O)<sub>2</sub>(15-TMC)]<sup>2+</sup> [17]. The Ru–O bond distances of Ru<sup>IV</sup>O complexes are *c.* 1.765 Å while those of Ru<sup>VI</sup>O complexes are near 1.70 to 1.71 Å for saturated ligands. If π-aromatic donors exist in the plane perpendicular to the Ru–O bond they will also promote elongation of the Ru–O bond [17]. These effects are in response to the filling of (d<sub>xy</sub>)<sup>2</sup>(d<sub>xz</sub>)<sup>1</sup>(d<sub>yz</sub>)<sup>1</sup> for d<sup>4</sup> Ru<sup>IV</sup> and the (d<sub>xy</sub>)<sup>2</sup> population for d<sup>2</sup> Ru<sup>VI</sup> in a symmetry generated either by RuO or Ru(O)<sub>2</sub> chromophores [28]. The population of (d<sub>xz</sub>)<sup>1</sup>(d<sub>yz</sub>)<sup>1</sup> orbitals which are antibonding in character in the molecular orbitals for these complexes promotes weakening and lengthening of the Ru<sup>IV</sup>O bond. Upon formation of the radicaloid intermediate, the weakened LRu<sup>IV</sup>O–(olefin)<sup>•</sup> intermediate, strongly favors rapid loss of the epoxide which also means that ring closure will be rapid compared to a potential rotational motion within the carbon-centered radical. Thus Ru<sup>IV</sup>O oxidants operate to epoxidize olefins with retention (group A).

The stronger Ru–O bond in Ru<sup>V</sup>–O and Ru<sup>VI</sup>–O species will disfavor O-atom motion toward the carbon radical center (i.e. ring closure). This creates a longer lifetime for Ru<sup>V</sup>–O–(olefin)<sup>•</sup> or Ru<sup>VI</sup>–O–O–(olefin)<sup>•</sup> intermediates. The stronger Ru–O unit and longer lifetime of the carbon-centered radical allows for competition between rotation toward the *trans* arrangement versus ring closure that produces both *trans*-oxide and *cis*-

oxide products from *cis*-stilbene or *Z*-olefins from Ru<sup>V</sup>–O and Ru<sup>VI</sup>–O oxidants. There are two viable orientations of approach of olefins (and stilbenes) which allow for positive net overlap between the olefin π cloud and the oxenoid p orbital that is also interactive with the π (d<sub>xz</sub>, d<sub>yz</sub>) orbitals on the Ru atom. These are the symmetrical approach side on for the olefin or an end-on attack which has multiple angular distributions (Scheme 3).

The symmetric pathway could not be discerned from the concerted (non-radical) addition which preserves stereochemistry of the epoxide product. Che and co-workers noted that the radicaloid intermediate could take on a range of chemical descriptions in response to the electronic effects of the carbon substituents [16]. Electron releasing groups would stabilize carbonium intermediates (pathway d of Scheme 1) or radicals (pathways b or c plus e in Scheme 1). Our evidence for the absence of carbonium rearrangement products [1] rules out path d for the [Ru(hedta)]/t-BuOOH



Scheme 3.

epoxidation of stilbenes. Thus only the radical intermediates versus concerted addition need be considered. We cannot know whether rotation ( $k_r$ ) is very rapid compared to ring closure  $k_c$  or  $k_c'$ . It may be that  $k_r \sim k_c$  ( $k_c'$ ) and that the *cis*-oxide/*trans*-oxide ratio reflects only this completion. However, if rotation was always very rapid such that  $k_r \gg k_c$  ( $k_c'$ ) then all of the *cis*-oxide product from *cis*-stilbene for catalysts of Group B would originate from the symmetric addition route. The product analysis for the [Ru<sup>III</sup>(hedta)]/t-BuOOH epoxidation of *cis*-stilbene puts an upper limit to the concerted pathway as 11 events out of 74 (14.9%). It is very likely that the competition  $k_r$  versus  $k_c$  contributes some of the *cis*-oxide formation. Thus the concerted pathway is at best a minor one in the [Ru<sup>III</sup>(hedta)]/t-BuOOH epoxidation.

Stereochemical purity in the epoxidation of stilbenes by Ru-oxo agents can only be achieved using Ru-O catalysts with crowded reactive sites that prevent rotation within radicaloid intermediates or by using Ru<sup>IV</sup>O catalysts with exposed terminal oxo groups and Ru-O interactions further weakened by  $\pi$ -aromatic N-donors. The unfortunate aspect of this is that these are also stronger oxidants due to the effect of weakening of the Ru<sup>IV</sup>-O bond. The product epoxides that are liberated are subjected to more oxidizing catalysts which often degrade the first product to aldehyde and carboxylic products (cf. the reactivities of [Ru(bpy)<sub>2</sub>(py)O]<sup>2+</sup> and [Ru(5,5'-Me<sub>2</sub>bpy)<sub>2</sub>(O)<sub>2</sub>] in Table 1).

Although it is possible that Ru<sup>VO</sup> complexes might exhibit intermediate behavior between Ru<sup>IV</sup>O and Ru<sup>V</sup>O complexes, the lone exception to the classifications given in this report is the recent data of Taqui Khan *et al.* concerning the epoxidation of stilbenes by [Ru<sup>VO</sup>(edta)]<sup>-</sup> [24]. The coordination environment of [Ru<sup>III</sup>(edta)]<sup>-</sup> and [Ru<sup>III</sup>(hedta)] and their oxo adducts should be virtually identical in ligand donor and steric effects. It seems likely that if the epoxidation behavior of [Ru<sup>VO</sup>(edta)]<sup>-</sup> were re-examined with *cis*-stilbene, that there may be a mixture of *cis*-oxide and *trans*-oxide products rather than the strict retention of *cis*-oxide stereochemistry which has been reported. However, it should be noted that the [Ru<sup>VO</sup>(edta)]<sup>-</sup> epoxidation data was obtained in a mixed solvent system (50:50 water:dioxane). It is possible that solvation effects might influence the accessibility of the Ru<sup>VO</sup> moiety, the orientation of approach of stilbenes, or even the rate of rotation ( $k_r$ ). A crowded coordination sphere of larger dioxane molecules in the vicinity of the radical might have the same effect as ligand-induced crowding of the decorated Ru (porphyrins). The influence of solvent composition on another reagent from Group B would be worthy of investigation in order to see if epoxidation stereochemistry could be readily altered in this manner.

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