Ru^{III}(hedta) as an oxygen atom transfer catalyst in the epoxidation of stilbenes

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Abstract

Ru^{III}(hedta) and $Ru^{III}((CH_3)_2edda)^+$ ($hedta^{3-}$ = *N*-hydroxyethylethylenediaminetriacetate; $(CH_3)_2edda^{2-}$ = *N,N'*-dimethethylethylenediamine-*N,N'*-diacetate) catalyze the epoxidation of *cis*-stilbene and *trans*-stilbene using tert-butylhydroperoxide (t-BuOOH) as the oxygen source. Prior spin-trapping studies have documented the existence of $LRu^{III}O \leftrightarrow LRu^{IV}O^{\cdot -} \leftrightarrow LRu^{V}O^{2-}$ character in the species obtained from $Ru^{III}L$ and to-BuOOH (L = polyaminopolycarboxylate ligands related to $edta^{4-}$). The O-atom complex, $LRu^{III}O$, appears responsible for the epoxidation of stilbenes. Yields as high as 63.5% *cis*-stilbene oxide plus 11.0% *trans*-stilbene oxide from *cis*-stilbene and 65.1% *cis*-stilbene oxide from *trans*-stilbene (with no *trans*-stilbene oxide) are formed in the epoxidation reactions. Secondary oxidations of the epoxide products produce between 4 to 8% benzaldehyde depending on conditions. The product distribution using the $Ru^{III}L$/t-BuOOH catalyst requires at least three epoxidation pathways: (i) concerted transfer of the oxenoid oxygen to the stilbene nucleophile; this process is favored for *cis*-stilbene; (ii) an outer-sphere electron transfer from the stilbene to $LRu^{III}O$ forming a carbon-centered cation radical adjacent to $LRu^{III}O^{\cdot -}$; this radical pair may couple directly for *cis*-stilbene or after a rapid isomerization of the *trans*-stilbene radical; (iii) an acyclic pathway which has both free radical and carbocation resonant character; this allows for isomerism of *cis*-stilbene to *trans*-stilbene oxide products. $Ru^{III}O$(hedta) is also observed to cleanly oxidize benzaldehyde to benzoic acid, *sec*-phenetyl alcohol to acetophenone, and benzyl alcohol to benzaldehyde and benzoic acid. Cyclohexene is hydroxylated and further oxidized to 2-cyclohexene-1-one.

Introduction

Ru^{III} polyaminopolycarboxylate complexes ($Ru^{III}L$; L = $hedta^{3-}$, $edta^{4-}$ and $ttha^{6-}$) react with tert-butylhydroperoxide (t-BuOOH) to give an intermediate having $LRu^{III}O \leftrightarrow LRu^{IV}O^{\cdot -} \leftrightarrow LRu^{IV}O^{2-}$ resonant character [1]. This species was spin-trapped using DMPO to give a unique EPR spectrum. It has been reported by Taqui Khan *et al.* that a complex formulated as $[(edta)Ru^{V}(O^{2-})]^-$ carries out O-atom transfer to triphenylphosphine [2], and is involved in the epoxidation of cyclohexene [3], and the oxidation of saturated hydrocarbons and alcohols [3]. We report herein that the $Ru^{III}L$/t-BuOOH system does not epoxidize cyclohexene, but rather forms 2-cyclohexene-1-ol and 2-cyclohexene-1-one. This brings to question whether the $Ru^{III}L$/t-BuOOH species is an η^2-alkylperoxo complex or whether O-atom transfer, forming authentic $LRu^{III}O \leftrightarrow LRu^{IV}O^{\cdot -} \leftrightarrow LRu^{V}O^{2-}$, occurs. If the latter is the proper description, $LRu^{V}O^{2-}$ does not epoxidize cyclohexene, but rather hydroxylates it. An η^2-alkylperoxo complex has been proposed as the oxidant of saturated hydrocarbons by $Ru^{II}(L')_2(H_2O)_2$ catalysts (L' = bipyridines and *ortho*-phenanthrolines) in combination with t-ButOOH [5b]. This system is inhibited by π-acid ligands which displace H_2O and stabilize Ru^{II}. Che has proposed a biradical complex, formally $(L')_2Ru^{I}$–O(Bu)–$O^{\cdot}$, to explain its activity [5b, 6]. Although the secondary ligand environment is much different with bipyridines and *ortho*-phenanthrolines, these studies identify the importance of determining whether oxo-ruthenium or alkylperoxo–ruthenium complexes are the proper description when ruthenium complexes activate t-BuOOH. Indeed, evidence herein support the conclusion that the secondary ligands, L = polyaminopolycarboxylate or L' = nitrogen heterocyclic ligands can exert a strong mechanistic influence in the pathway for t-BuOOH oxidations as catalyzed by RuL centers.

Both η^2-alkylperoxo complexes ($LM(OOR)^{n-1}$) and the metal oxo species derived from O-atom transfer by ROOH to LM^{n+} (LMO^{n+}) epoxidize olefins stereoretentively via metallocyclic intermediates [4, 5]. Either route is non-radical in character and leads to high stereoselectivity and specificity [4, 5]. It is possible in some cases to identify the presence of the LMO^{n+} form when isomerism accompanies the epoxidation of

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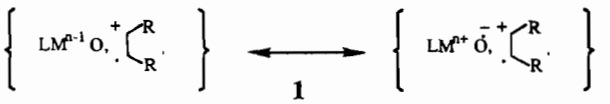
the olefin by an electron transfer pathway which may operate in parallel with the non-radical concerted and metallacyclic routes. A caged radical pair (**1**) with resonance allows for rearrangement prior to collapse of the cage pair to products [7, 10, 11]



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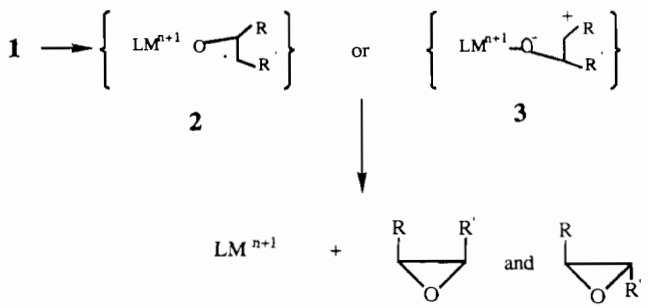
This process may involve the rotation of the central bond in the radical cation prior to trapping by the metal oxenoid partner or by addition at the olefinic carbon. The latter route yields an acyclic radical (**2**) or carbocation (**3**) which may rotate prior to ring closure forming the epoxide isomers.



Little evidence exists for an electron transfer pathway in the epoxidation of olefins by η^2-alkylperoxide complexes which epoxidize olefins with retention of stereochemistry [4, 5].

In this study we report on the reaction of $Ru^{III}L$ plus t-BuOOH with *cis* and *trans*-stilbene as a test of the presence of a metal oxenoid intermediate. It is observed that the intermediate possesses a reactivity toward *cis* and *trans*-stilbene comparable to several P-450 models [6–16] and bleomycin [17–19] toward stilbenes and styrenes. In the epoxidation of styrenes and stilbenes there exists evidence for an electron transfer activated intermediate **1** leading to **2** and/or **3** in the metalloporphyrin catalyzed epoxidations [6, 7, 10, 11] and for the bleomycin-mediated epoxidations [18, 19]. Thus the $Ru^{III}L$/t-BuOOH catalyzed epoxidation of *cis*- and *trans*-stilbene follows the behavior of other known oxenoid oxygen transfer agents, and not those of η^2-aklylperoxo complexes. An even greater percentage of electron transfer pathway is observed for the $Ru^{III}O$(hedta) complex than for metalloporphyrin catalyzed epoxidations, based on a much higher activity toward *trans*-stilbene for $Ru^{III}O$(hedta). Epoxidation of *trans*-stilbene occurs with complete isomerism to the *cis*-epoxide. These results are in general agreement with the stabilizing influence of $Ru^{III,\ IV,\ V,\ VI}$ on the oxo chromophore [12–14, 21–36] and the frequently observed 2-cyclohexene-1-one product from cyclohexene oxidations [37, 38].

Experimental

Reagents

cis-Stilbene, *trans*-stilbene, *sec*-phenethyl alcohol, benzaldehyde, cyclohexene, benzoic acid, 2-cyclohexene-1-one, styrene, acetophenone, cyclohexene oxide, methylene chloride, $K_2[RuCl_5(H_2O)]$, hydrogen peroxide (30%), OXONE = $(KHSO_5)KHSO_4 \cdot K_2SO_4$ and tert-butyl hydroperoxide (t-BuOOH) 90% were obtained from Aldrich. $K[Ru^{III}$(hedta)Cl] was prepared as described by Bajaj and van Eldik [39] (see below) and $Na[Ru^{II}(hedta)(H_2O)] \cdot 4H_2O$ as previously reported by us [1]. The observed epoxidation activity toward stilbene was independent of whether $K[Ru^{III}$(hedta)Cl] or $Na[Ru^{II}(hedta)(H_2O)] \cdot 4H_2O$ was used. It is well known that the Ru(hedta)Cl^- ions is rapidly aquated, forming $Ru^{III}(hedta)(H_2O)$, in solution [39]. This species is termed Ru^{III}(hedta) throughout the remainder of this text whereas Ru(hedta)$^-$ refers to the Ru^{II} complex ion, $Ru^{II}(hedta)(H_2O)^-$.

$K[Ru^{III}$(hedta)Cl] was prepared following the procedures described by Bajaj and van Eldik [39]. 0.50 g $K_2[RuCl_5H_2O]$ (1.33 mmol) was put into a 50 ml round-bottom flask containing 10 ml of 0.001 M $HClO_4$. 0.506 g Na_3hedta in 15 ml of 0.001 M $HClO_4$ was added to the flask. The solution was refluxed for about 2 h, followed by rotary evaporation to a small volume of about 5 ml. Ethanol was added to precipitate a yellow solid. The latter was filtered and washed with a cold water–ethanol (1:9) mixture, and dried in a vacuum oven at 25 °C. Proof of the identity of the product was carried out by comparison with literature parameters [37] and by reduction of known weights of the solid dissolved in water over Zn/Hg. The amount of Ru^{II} present was analyzed by addition of 2-methylpyrazine [1] and by the electrochemical behavior of the aquated sample in the presence of various π-acceptor substrates (pyrazine, CO, and olefins) [40]. Confirmation of the respective $Ru^{II}(hedta)L^-$ complex was made by CV/DPP procedures as described previously [40, 41]. $[Ru^{II}((CH_3)_2edda)(H_2O)_2]$ required synthesis of the ligand. The preparation of the *N,N'*-dimethyledda ligand proceeds smoothly from H_2edda [42, 43]. This subject will be reported separately in another paper which discusses the selectivity of $Ru^{II}((CH_3$edda) toward the coordination of olefins and pyrimidine bases [43, 44]. Satisfactory analytical data and NMR spectra for the $Ru^{II}((CH_3)_2edda)(H_2O)_2$ complex were obtained. The NMR spectra show a symmetrical *cis*-O (*trans*-diqua) complex with a planar N_2O_2 donor set from the *N,N'*-dimethyledda^{2-} ligand (see figure on p. 221).

Characterization methods

IR spectra for confirmation of ruthenium salts and organic reactants and products were obtained in KBr pellets pressed at 9 tons, or between NaCl plates. These spectra were recorded on IBM IR/32 FTIR and Cignus Mattson-100 FTIR instruments using 64 averaged scans. ^1H and ^{13}C NMR spectra were recorded on a Bruker AF 300 NMR or AF 500 NMR spectrometer at magnetic fields of 70.46 and 117.44 kG, respectively. ^1H spectra employed frequencies of 300.13 and 500.13 MHz, respectively. ^{13}C spectra were obtained at 125.767 MHz at the 117.44 kG field. All spectra of ruthenium complexes were obtained on Ru^{II} complexes under Ar in D_2O. These complexes were obtained by a prior 2 h reduction over Zn/Hg to remove Ru^{III} paramagnetic impurities. Ar flushed NMR tubes were filled by syringe techniques to obtain spectra of the Ru^{II}(hedta) complex for purity checks. The reference was HOD or DSS. The organic reagents were examined in $CDCl_3$ using TMS or an internal organic compound of known chemical shift as a reference. The identity of a presumed product in the reaction mixture was assigned by a combination of standard decoupling, integration and standard addition techniques. The reference for ^{13}C spectra was *p*-dioxane. A standard 14-H broad-band decoupling was used for ^{13}C spectra. The amount of the products and unconsumed stilbene reactant was determined by integration of the product solution after extraction into $CDCl_3$ in comparison with CH_2Cl_2, added as an inert reference. The reactant and CH_2Cl_2 were integrated from both initial and final solutions as described below.

Oxidation reactions

In a typical experiment, 0.15 ml (1.35×10^{-3} mol) of 90% t-BuOOH was added to an $\sim10^{-3}$ M solution of Ru(hedta)$^-$ (8×10^{-4} g, 1.65×10^{-6} mol) in 2 ml of H_2O in a glass vial with a rice-size stirring bar. The reaction mixture was stirred at room temperature for 15 min, then 6.0×10^{-2} ml (3.26×10^{-4} mol) of *cis*-stilbene and 5.0×10^{-2} ml of methylene chloride, CH_2Cl_2, (7.75×10^{-4} mole as the internal standard) were added to the mixture. The vial was sealed with a polyethylene cap, further wrapped with parafilm, and the mixture was stirred for 4 h. When the 4 h reaction time was over, 1.0 ml of chloroform-d $CDCl_3$ was added to the vial to extract the products from the reaction mixture in the H_2O solution. An appropriate sample was transferred to an NMR tube by filtration of the $CDCl_3$ extract through a Kim-wipe plug in a glass dropper pipet. This filtration removed particulate matter (if any) and water droplets from the organic sample.

Results and discussion

Reaction products from cis-stilbene

The products of the ruthenium-catalyzed reaction between t-BuOOH and stilbene were determined by ^1H NMR spectra. The *cis*-stilbene has a low solubility in water and the reaction mixture is heterogeneous. Resonances for unreacted *cis*-stilbene (7.23 and 6.60 ppm) and CH_2Cl_2 (5.30 ppm) as internal standard were identified in the $CDCl_3$ product solution's spectrum. The distinct ^1H resonances for *cis*-stilbene oxide at $H_a = 3.88$ ppm, $H_b = 7.39$ ppm were observed. In addition to *cis*-stilbene oxide, other oxidation products, (*trans*-stilbene oxide, 4.36 ppm; styrene oxide, 2.8 to 3.9 ppm; and benzaldehyde, 10.01 ppm) were also observed. Blank experiments established that no *cis*-stilbene oxide was formed from the combination of *cis*-stilbene and t-BOOH in the absence of Ru^{II}(hedta)$^-$ catalyst under the same conditions. Epoxidation did not take place for the combination of *cis*-stilbene and Ru^{II}(hedta)$^-$ under O_2 without t-BOOH.

The calculations of percent yields were based on the integrations on hydrogen peaks from unreacted *cis*-stilbene, benzaldehyde, *trans*- and *cis*-stilbene oxide by ^1H NMR. CH_2Cl_2 served as an internal integration standard. The percent yields of *cis*-stilbene oxide varied from 6.5% to ~65.7% depending on the reaction conditions (see Table 1). Water soluble products such as benzoic acid would not be determined by this technique; similar data reduction methods have been used by other workers in the field when aqueous samples are involved (e.g. the studies of Hecht and co-workers [18, 19] and Castellino and Bruice [10]). Therefore the

TABLE 1. Product yields and material balance for the oxidation of *cis*-stilbene with t-BuOOH catalyzed by Ru(hedta)$^-$ in H_2O

Amount of Ru^{III}(hedta) (mol)	Yield (%)			
	cis-stilbene (unreacted)	*cis*-oxide	*trans*-oxide	PhCHO
5.73×10^{-7}	24.7	45.7	6.6	4.2
1.15×10^{-6}	5.4	60.0	11.6	4.3
1.23×10^{-6}	1.7	63.5	11.0	5.6
1.71×10^{-6}	14.9	45.9	17.4	3.1
2.86×10^{-6}	13.0	49.5	10.6	8.2
4.10×10^{-6}	20.1	43.4	11.3	6.5
5.36×10^{-6}	23.6	38.8	10.9	6.6
8.30×10^{-6}	40.5	37.1	6.9	7.9
1.20×10^{-5}	44.9	22.8	8.6	5.0
2.43×10^{-5}	64.8	11.4	1.7	3.3
4.10×10^{-5}	68.4	6.5	3.9	2.4
4.76×10^{-5}	70.0	5.8	1.1	4.4

The reactions employed 1.35×10^{-3} mol of t-BuOOH, 3.26×10^{-4} mol of *cis*-stilbene and 7.75×10^{-4} mol of methylene chloride in 2 mol of H_2O. Reaction time = 4 h.

product formation of epoxides and aldehydes may be compared reasonably with the former studies of these research groups. Our mass balance of 81% is nearly the same as that of Castellino and Bruice [10] (76%) under similar conditions.

Reaction products from trans-stilbene

When *cis*-stilbene was reacted with t-BOOH catalyzed by Ru(hedta)(II or III) or $Ru^{II}((CH_3)_2edda)$, there was always some *trans*-stilbene oxide observed. When *trans*-stilbene was reacted with t-BOOH catalyzed by Ru(hedta)(II or III) or Ru^{II}(*N,N'*-dimethyledda), only *cis*-stilbene oxide was detected (see Table 2) in high yield.

Epoxidation sensitivity to O_2 and CO

Several experiments were carried out in the absence of air with Ar, O_2 or CO present as the gas phase to investigate aspects of the oxygen activation cycle for Ru^{III}L/t-BuOOH epoxidations of *cis*-stilbene (Table 3).

The results in Table 3 show that the yields under Ar, O_2 or CO are similar to the data in Table 1 with air exposed samples. The following conclusions may be drawn. (i) The epoxidation of stilbene and t-BuOOH catalyzed by Ru(hedta) is virtually O_2 independent. (ii) $Ru^{II}(hedta)^-$ must first be oxidized to the form of Ru^{III}(hedta) as the minimal oxidations state to take part in the reaction cycle. This is confirmed by the reaction scavenged under CO. If the 2+ state of Ru^{II}(hedta) is involved in one of the steps of the oxidation and reduction of Ru(hedta) in the reaction cycle, then CO would react with $Ru^{II}(hedta)^-$ to a form which should greatly reduce the yield of the *cis*-stilbene oxide, or even terminate the epoxidation reactions. The results showed that CO did not depress the yield of the epoxidation reactions. (iii) The yield of benzaldehyde does not increase significantly with O_2 saturation compared to CO and would appear to originate from some other pathway than one requiring the presence of O_2.

TABLE 2. Product yields of epoxidation of *trans*-stilbene catalyzed by Ru(hedta)(II and III) and Ru(*N,N'*-dimethyledda)

Amount of catalyst (mol)	Yield (%)			
	trans-stilbene	*cis*-oxide	*trans*-oxide	PhCHO
1.54×10^{-6} [a]	20.3	45.6	0.0	4.0
1.48×10^{-6} [b]	19.8	49.1	0.0	1.0
1.64×10^{-6} [c]	17.7	65.1	0.0	6.2

[a] $Ru^{II}(hedta)^-$ as starting catalyst. [b] Ru(*N,N'*-dimethyledda) as catalyst. [c] Ru^{III}(hedta) as starting catalyst. All other reagents are the same as Table 1.

TABLE 3. Product yields of the epoxidation of *cis*-stilbene and *trans*-stilbene catalyzed by Ru(hedta) and Ru(*N,N'*-dimethyledda) under different conditions

	Yield (%)			
	cis-stilbene (unreacted)	*cis*-oxide	*trans*-oxide	PhCHO
Under CO	18.3	56.5	21.4	3.8
Under Ar [a]	36.2	52.8	10.5	0.5
Under Ar [b]	15.8	48.0	12.2	5.2
Under O_2	18.7 [d]	53.1	11.2	2.9
Under Ar [c]	7.8	53.2	4.0	7.8

[a] Starting from $NaRu(hedta)\cdot4H_2O$/t-BuOOH added prior to substrate. [b] Starting from $Ru^{III}(hedta)(H_2O)$. [c] $Ru^{II}((CH_3)_2$-edda) as catalyst; others with Ru^{III}(hedta) as catalyst. The reactions employed $[Ru]_{total} = 1.7\times10^{-6}$ mol, 1.35×10^{-3} mol of t-BuOOH, 3.26×10^{-4} mol of stilbenes and 7.75×10^{-4} mol. [d] Average of two runs.

Comparison with related systems

The results from product analyses from the Ru^{III}(hedta)/t-BuOOH catalyzed epoxidation of *cis*- and *trans*-stilbene are compared in Table 4 with a number of related studies using metallobleomycin, M(BLM), and metalloporphyrin catalyzed epoxidations of these olefins. The variability of solvent system, solubilities, modes of olefin addition, and reaction times of the separate studies limit the discussion to some general, but important, observations. The *cis*-stilbene isomer is much more reactive in all cases. The presence of the *trans*-stilbene oxide from *cis*-stilbene requires the operation of pathways having radical character [6–22]. This implicates the presence of the $Ru^{III}O$(hedta) species.

When detected, deoxybenzoin as a product is postulated as a signature rearrangement product via the carbocation intermediate **3** [3–22]. Rearrangement does not compete with epoxidation for the Ru^{III}(hedta)/t-BuOOH system. The formation of benzaldehyde has been attributed to scavenging of **1** by O_2 in some of the studies [10, 17–19]. The results from Table 3 show that this explanation is not appropriate for the Ru^{III}(hedta)/t-BuOOH pathway which forms benzaldehyde.

Our results show that Ru^{III}(hedta)/t-BuOOH is a more active catalyst for stilbene epoxidations than either Fe^{III}(BLM) or Cu^{II}(BLM) using iodosylbenzene (ϕIO), but less active than $Mn^{III}(TPP)Cl/\phi IO$ in CH_2Cl_2.

The most striking result comes from the comparison of the epoxidation of *trans*-stilbene. *trans*-Stilbene is often much less reactive (usually by a factor of 10 or more) for other catalysts as exemplified in Table 4. Expoxidation usually proceeds with retention of configuration in low percentage yields. Ru^{III}(hedta)/t-BuOOH is a much more active catalyst towards *trans*-stilbene, converting 65% of *trans*-stilbene to the *cis*-

TABLE 4. Comparison of product analysis for stilbene epoxidations

Catalyst/oxidant	Solvent system	From *cis*-stilbene				From *trans*-stilbene				Reference
		cis-oxide	*trans*-oxide	DEB	ϕCHO	*cis*-oxide	*trans*-oxide	DEB	ϕCHO	
Ru^{III}(hedta)/*t*-BuOOH	H_2O	49.5	10.6	0	8.2	65.1	0.0	0	6.2	this work
Fe^{III}(BLM)ϕIO	91%CH_3OH/9%H_2O	22–25	1	7	5	0	3	2	NR	19b
Cu^{II}(BLM)ϕIO	91%CH_3OH/9%H_2O	3–7	1	1	NR	<1	1	2	NR	19c
Mn^{III}(BLM)/ϕIO	95%CH_3OH/5%H_2O	9	2	15	1	NR	NR	NR	NR	
Fe^{III}(TPP)Cl/ϕIO	90%CH_3CN/10%H_2O	39	1	1	1	NR	NR	NR	NR	19b
Fe^{III}(F_{20}TPP)Cl/$F_5\phi$IO	CH_2Cl_2	42.4	1.5	1.5	5.0	0	5.3	0.1	NR	10
Mn^{III}(Cl_8TPP)OH/$F_5\phi$IO	CH_2Cl_2/CH_3OH/H_2 (80:18:2)	33.7	1.8	1.5	0		2.5	0	NR	10
Mn^{III}(TPP)Cl/ϕIO	CH_2Cl_2	33	55	NR	NR	NR	NR	NR	NR	20
Mn^{III}(OCH_3)$_4$TPP)Cl/ϕIO	CH_2Cl_2	64	23	NR	NR	NR	NR	NR	NR	20
Mn^{III}(TPP)Cl/LiOCl	CH_2Cl_2	35	5.2	NR	NR	NR	NR	NR	NR	4b

NR = not reported in the reference.

epoxide in the same reaction time. Thus the reactivity of Ru^{III}(hedta)/t-BuOOH is 20 to 30 times greater than the other epoxidation catalysts, but with isomerism accompanying epoxidation. A major difference between $Ru^{III}O$(hedta) and the metallobleomycin and metalloporphyrin catalysts is the physical size of complex and the extent of exposure toward the olefin as it approaches an activated oxygen. Epoxidations by metalloporphyrins clearly show that the reactivity towards *cis*-stilbene (and styrenes) decrease as the peripheral substituents increase in steric crowding of the LMO^{n+} chromophore [6–20]. Prior work has shown that Ru^{II}(hedta)$(H_2O)^-$ and $Ru^{II}((CH_3)_2edda)(H_2O)_2$ have very exposed 'NO_3' faces for the approach of an olefin. The Ru^{II} forms are, in fact, excellent coordination complexes for the binding of η^2-olefins and pyrimidines [40]. One of two possible isomers which has a NO_3 face for Ru(hedta)(H_2O) and a related isomer of $Ru((CH_3)_2edda)(H_2O)_2$ are shown below. The normal geometry for $Ru^{II}((CH_3)_2edda))(H_2O)_2^{2+}$ has equivalent glycinato chelate rings as shown by ^1H NMR but the more open isomer having the NO_3 face is readily achieved by an equilibrium in solution [43, 44].

Ru^{II}(hedta)(H_2O)

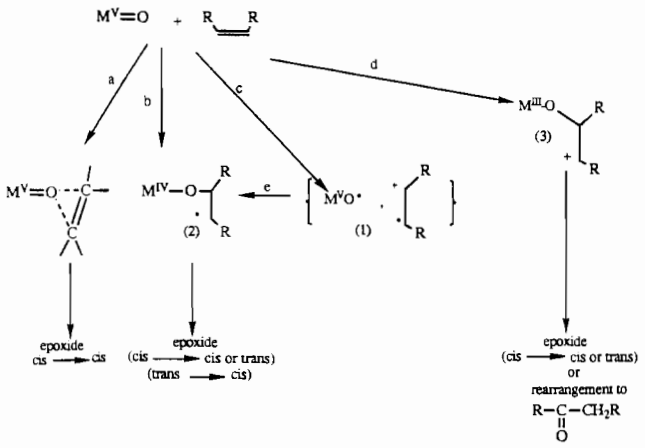
hindered isomer more-open isomer

$Ru^{II}((CH_3)_2edda)(H_2O)_2$

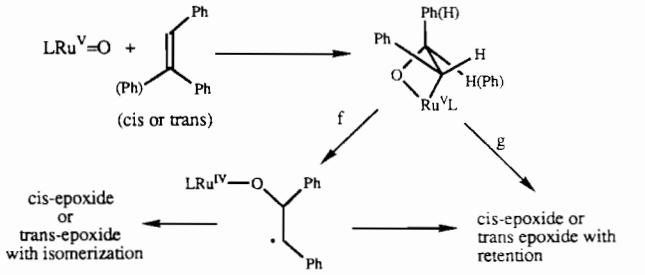
Conclusions on the epoxidation mechanism

The characterization of the organic products is sufficient to provide a qualitative picture which requires ruthenium(V)–oxo ↔ ruthenium(III)–oxene activity and not that of an η^2-alkylperoxide. Plausible stepwise mechanisms for Ru(hedta)-catalyzed epoxidation parallel those already shown by the combination of the scheme of Bruice [10] with that of Collman *et al.* [6, 7] with metalloporphyrin systems (Scheme 1).

Acyclic pathways of radical or carbocation character are required to explain the formation of *trans*-stilbene and its oxide from *cis*-stilbene for the Ru(hedta)-cat-



Scheme 1.



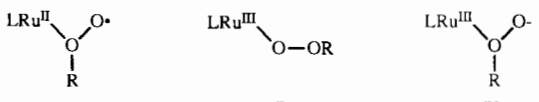
Scheme 2.

alyzed system, just as observed with metalloporphyrin-catalyzed epoxidations [6–14]. The acyclic pathways alone cannot explain the fact that the only *cis*-stilbene oxide is obtained from *trans*-stilbene. The reaction of *trans*-stilbene with t-BuOOH catalyzed by Ru(hedta) must proceed through a different pathway from the dominant path used by *cis*-stilbene. A metallocyclic route has been suggested as a possible olefin epoxidation channel [4, 5]. A metallocyclic pathway should proceed as shown in Scheme 2.

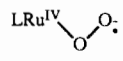
It has been noted by Castellino and Bruice [10] that *cis*- and *trans*-stilbene should epoxidize with retention via path g in competition with isomerization to only a minor extent via ring opening as in path f of the diagram. Therefore even the often-proposed metallacyclic pathway for olefin epoxidations fails to account for the purity of *trans*-stilbene to *cis*-stilbene oxide conversion.

The probable explanation rests on the outer-sphere electron transfer pathway via **1**. Assuming the stilbenes approach the M=O group on the side as shown by computer modeling and as required for best overlap of olefin and oxenoid [7], it is clear that only the *cis*-stilbene approaches closely enough for efficient use of the concerted addition at oxygen (path a, Scheme 1), or the direct addition to yield acyclic intermediate radicals (path b, Scheme I). Path b is the equivalent of a very rapid capture of intermediate **1** prior to rotation via steps c and e. However, *trans*-stilbene must form the radical pair **1** at longer distances due to its hindered approach by either the NO_3 plane of RuO(hedta) or the N_4 porphyrin plane of the porphyrin catalysts. The radical pair **1** formed by *trans*-stilbene would have longer time for a rotation within the radical cage. Rotating the phenyl ring up will then allow the easier approach shared by *cis*-stilbene, but rate limited by the rotation. This route (path e) will give only *cis*-stilbene oxide from either *cis*- or *trans*-stilbene. The difference for *cis*-stilbene in providing a pathway to the *trans*-epoxide is its ability to utilize a more direct addition at one carbon in the reaction progress profile via path b. This allows for a mixture of *cis*- and *trans*-epoxides, but the main pathway of concerted addition (via a, prevented for *trans*-stilbene) gives an overall much higher yield of *cis*-epoxide versus *trans*-epoxide from *cis*-stilbene.

That the only reasonable route for *trans*-stilbene epoxidation requires the electron transfer pathway and that *cis*-stilbene may utilize the concerted, an acyclic addition, and the electron transfer pathways establishes that the form of the ruthenium catalyst is a metal oxo species not an η^2-alkylperoxide. Other possible structures including alkylperoxy radicals (**4**), η^1-alkylperoxides (**5a**, **5b**) and superoxo species (**6**). $H_2O_2/Ru^{III}L$ does not lead to epoxidation although $LRu^{II}(O_2^{-}\cdot)$ species have been spin-trapped in prior studies [1].



4 **5a** **5b**



6

This rules out **4** as an active intermediate. The radical character associated with the isomerism pathways which accompany epoxidation rule out either η^1 or η^2 species as the active agents; this eliminates **5a** or **5b**. Superoxo complexes (**6**) are not involved because the yields of epoxidized products did not increase when O_2 saturated conditions were used, nor did yields decrease under Ar or CO. The absence of an effect of CO also rules out **4** as an intermediate as these should react rapidly with CO.

Influence of precursor catalyst concentration

The issue of whether the epoxides undergo further oxidation is described in the next section of this report. However, it can be seen in Table 1 that the amount of unreacted *cis*-stilbene increases steadily above 6.15×10^{-4} M catalyst (third entry of Table 1). In our

prior report [1] we showed that Ru^{II}(hedta) may be oxidized to a binuclear Ru^{IV}_2(hedta)$_2$ complex. Furthermore an oxo-bridged, mixed oxidation state (III, IV) complex, $Ru_2O(edta)_2^{3-}$, has been recently reported by Hurst and others [45]. We have observed that a mixed-oxidation state Ru_2(III, IV) complex may also be prepared from Ru^{III}(hedta) by prolonged stirring with air. The binuclear complexes have no labile coordination sites for t-BuOOH.

When Ru^{III}(hedta) was air oxidized, forming large amounts of the Ru_2(III, IV) complex, and this solution was then compared directly against an equivalent Ru^{III}(hedta) sample untreated with O_2 (air) in water, the system containing the Ru_2(III, IV) binuclear ion with t-BuOOH had less than 15% of the activity for the epoxidation of *cis*-stilbene. This leads to the conclusion that the binuclear oxo-bridged species are inactive*. This is in agreement with the absence of $LRu^{IV}O$ species being detected by the spin-trapping method when t-BuOOH is present with Ru^{IV} binuclear complexes [1]. Ru_2(III, IV) binuclear complexes might form by the reaction of $Ru^{II}(hedta)^-$, formed during benzaldehyde oxidations as described in the next section, and from $Ru^{III}O$(hedta). The bimolecular process (Ru^{II} and $Ru^{V}O^{2-}$) will form oxo-bridged Ru_2(III, IV) binuclear products which are relatively inactive. The dissociation equilibrium of Ru_2(III, IV) into monomeric Ru^{III}(hedta) and Ru^{IV}(hedta) controls the available pool or Ru^{III}(hedta). Another route to inert, bridged Ru_2(IV, IV) dimers could be the combination of Ru^{III}(hedta) and $Ru^{V}O$(hedta); the encounter of these species would increase with ruthenium concentration. A saturation in the amount of unreacted *cis*-stilbene is observed (Fig. 1) at high total Ru^{III}(hedta), indicative of a limited pool of available active catalyst.

The action of Ru(hedta) delivers an oxygen atom to stilbene. Ru^{II}(hedta) or Ru^{III}(hedta) must be first oxidized to V (e.g. III-O atom) as discussed above, and then they participate in the catalytic oxygen atom transfer reaction.

The relationship between catalytic efficiency and total Ru present has been tested. We have observed a marked effect of the total concentration of Ru on the yield of epoxidation of *cis*-stilbene (see Fig. 2).

From Fig. 2 and Table 1, it can be seen that the yield of *cis*-stilbene oxide is increased with the amount of Ru(hedta) at low concentration of Ru(hedta). When the concentration of Ru(hedta) increases further, an apparent maximum yield occurs at 63.5%. The yield of *cis*-stilbene oxide declines above this critical value. This decline at higher total Ru level seems to reflect

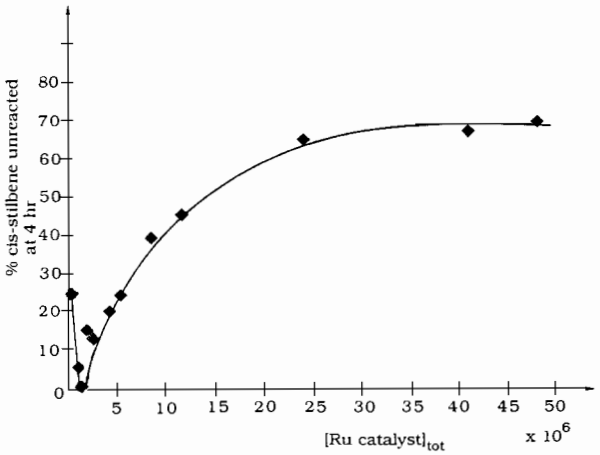


Fig. 1. Saturation in unreacted *cis*-stilbene with Ru(hedta) catalyst concentration: $[t\text{-BuOOH}]_i = 0.675$ M; stilbene available = 3.26×10^{-4} mol; $T = 22$ °C; air saturated.

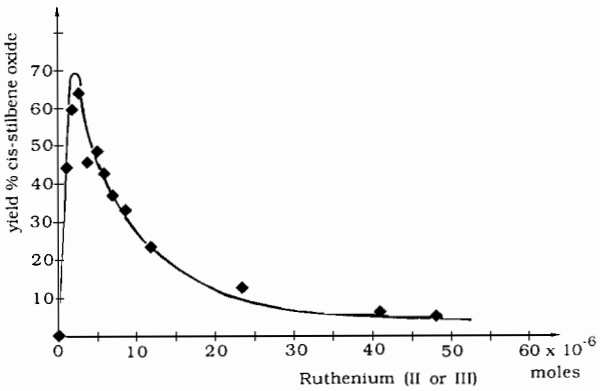
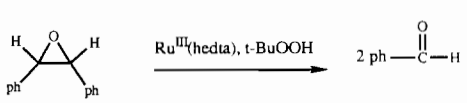


Fig. 2. Yield of *cis*-stilbene oxide with amount of Ru(hedta) catalyst: [t-BuOOH] = 0.675 M; stilbene available = 3.26×10^{-4} mol; $T = 22$ °C; air saturated.

the result of a further oxidation of the products when more $Ru^{V}O$(hedta) is available.

Diagnostic oxidations of related organic compounds

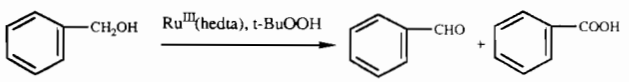
The following reactions have been studied to investigate the origin of the decline of yield of the epoxide products together with an increase in benzaldehyde with the increase of the Ru(hedta); see eqns. (1) to (6)**. The indicated products were identified by ^1H and ^{13}C NMR for each reaction. At high total Ru^{III}(hedta) both epoxidation and benzaldehyde formation decrease together. This suggests that benzaldehyde formation requires prior formation of either *cis*- or *trans*-stilbene oxide.



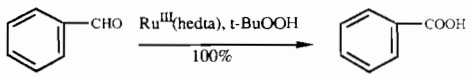
(1)

*Binuclear Ru^{III}_2O and $Ru^{III}ORu^{IV}$ species are also inert in the electrochemically catalyzed oxidation of primary and secondary alcohols.

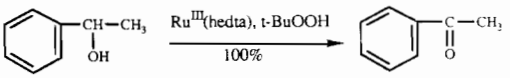
**All oxidations reported were shown to be absent with Ru^{III}(hedta) alone; t-BuOOH was required for reactivity.



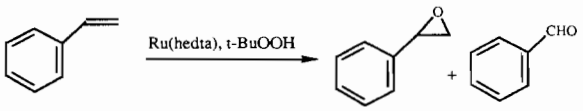
(2)



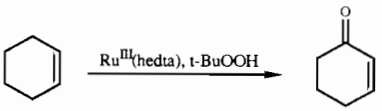
(3)



(4)



(5)



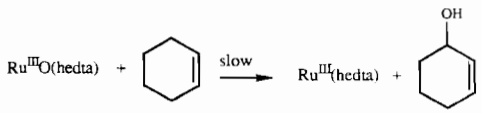
(6)

Similarly as reported in Table 1, there is an increase in the yield of benzaldehyde together with an increase in the epoxidation of either *cis*- or *trans*-stilbene. *cis*-Stilbene oxide forms benzaldehyde (eqn. (1)) in the presence of the Ru(hedta)/t-BuOOH catalytic system. Thus benzaldehyde is logically formed from either stilbene oxide (or its diol hydration production) during the reaction in competition with the initial epoxidation process. This subsequent oxidation of the original product appears to be important as well for the styrene epoxidation by Ru(hedta)/t-BuOOH (see eqn. (5)).

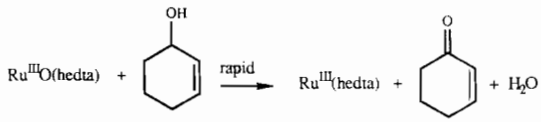
Collman *et al.* have detected phenylacetylaldehyde as a primary product, not by rearrangement of the styrene epoxide with Mn^{III} porphyrin oxidation catalysts [8]. They have described how this product may be achieved directly from the metallacyclic type of intermediate or from a pinacol rearrangement mechanism described by Groves and Myers [47]. The latter process was discounted by Collman *et al.* [8] based on the small substituent effects on substituted styrenes. In contrast, the formation of benzaldehyde must be due to a secondary oxidation process following the initial epoxidation for Ru(hedta)-catalyzed reactions. Any pathway yielding the related $PhCH_2(C{=}O)Ph$ product (deoxybenzoin) which would parallel the pathway which forms phenylacetyladehyde for porphyrin catalyzed epoxidation, is absent, based on ^1H NMR spectra of the RuO(hedta) epoxidized product solution. Only minor amounts of deoxybenzoin were detected by Hecht and co-workers in their study of Fe^{III}-BLM mediated epoxidation of stilbenes ($\leqslant 7\%$) [18, 19] or by Castellino and Bruice with Fe^{III}(porphyrin) catalysis ($\leqslant 1.5\%$) [10] or in the work of Collman *et al.* with Mn^{III}(porphyrin) ($\leqslant 3\%$) [8]. If this route involves the strained metallacyclic intermediate as suggested earlier by Collman *et al.* [8] it is not surprising that even lower yields would be found with the more hindered stilbenes relative to styrenes. This would make it reasonable that this route is very unfavorable for stilbene epoxidations and, if active, may form products below the limit of ^1H NMR detection.

Additionally, benzyl alcohol is further oxidized to benzaldehyde and benzoic acid (reactions (2) and (3)). There will be a competition in rates for the formation of epoxide products and their destruction via reactions (1) and (3). Since about 20% of the total organic products remain in undetected forms in our work and in those of former workers with the P-450 models and bleomycin-mediated epoxidation, it seems likely that much of the product oxidation results in formation of the water soluble benzoic acid.

The oxidation of secondary alcohols by $Ru^{IV}O$ catalysts is well known [25–29]. For example, the bipyridine-based $[(bpy)_2pyRu^{IV}O]^{2+}$ complex of Meyer and co-workers has been throughly studied and shown to promote alcohol oxidation by hydride transfer from the α-CH unit in the case of 2-propanol and other primary or secondary alcohols [21–23]. RuO(hedta) also carries out similar processes (eqns. (3) and (4)). Like Meyer's reagent which oxidizes cyclohexene to 2-cyclohexene-1-one [37], RuO(hedta) executes the same oxidation. The lability of Ru polyaminocarboxylates precludes detection of intermediates, but it would appear most probable that the formation of 2-cyclohexene-1-one occurs in two steps:

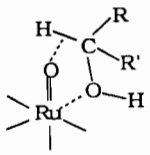


(7)



(8)

In a separate experiment, t-BuOH was shown to be inert to oxidation by RuO(hedta) which supports the need for an α-hydrogen adjacent to the hydroxyl oxygen for a hydride-like β-transfer to the RuO moiety. Cundari and Drago [48] have recently performed molecular mechanics calculations which support the best pathway of these alcohol oxidations by $Ru^{IV}O$ complexes as occurring by the side-on attack of the C–H bond with a stabilizing coordination of the alcohol oxygen at the Ru center:

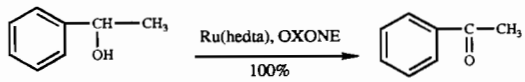


This is interesting in regard to the concerted or electron transfer-addition pathway of stilbenes described above, allowing for the Ru^{III}, Ru^{IV} and Ru^{V} character of the intermediate in the RuO(hedta) system. In both cases a region of electron density (the filled πMO of the olefin or σ filled orbital of C–H) is brought nearly orthogonal to the Ru=O bond. Electron transfer, followed by O insertion occurs for epoxidation for olefins. Similarly α-hydride transfer from an α-CH of an alcohol, instead of a one-electron step, may be facile. The product will be the stable ketone or aldehyde for alcohol, whereas the stilbenes must add an oxygen ligand to preserve the coordination number of 4 at carbon; otherwise the paths are similar.

The oxidation of the β-CH bond in cyclohexene deserves some comment. The epoxidation of the olefinic unit is not competitive with allylic oxidation. Using molecular models to illustrate the approach of the olefin chromophore toward the Ru=O bond of RuO(hedta), it is observed that the β-CH bond enters at a distance not significantly greater than the $\rangle C{=}C\langle$ fragment. The C–H bond is also simultaneously directed orthogonal to the RuO moiety. Thus, the olefin placement during the same approach which would be used for the concerted epoxidation or the outer-sphere olefin electron transfer route for stilbene and styrenes, places the allylic hydrogen of 1-cyclohexene in relatively the same orientation as the α-CH of secondary alcohols.

Meyer and co-workers [37] have noted that H atom (or D) abstraction of the allylic hydrogen by $[(bpy)_2pyRu^{IV}O]^{2+}$ must be followed by capture of the same position by OH, as in a rebound pathway, more rapidly than an allylic rearrangement or escape of the radical from the solvation cage in the oxidation of 3,3,6,6,-d_4-cyclohexene. The kinetic isotrope effect of 18 for H versus D strongly suggests the rebound hydroxylation in the first step in the system of Meyer and co-workers [37]. We have not performed kinetic studies because no spectrally detectable intermediate was observed when RuO(hedta) serves to oxidize cyclohexene. Using $[(bpy)_2pyRuO]^{2+}$, Meyer and co-workers were able to observe kinetically separable oxidation steps with a coordinated 2-cyclohexene-1-ol bound by Ru^{III}. Its internal alcohol oxidation forming 2-cyclohexene-1-one and Ru^{II} was slow, and the process could be followed spectrophotometrically. In our study the reaction phase is heterogeneous and precludes similar or related observations. However, the absence of the epoxide or the 2-cyclohexene-1-ol in the ^1H NMR spectrum of the products suggests parallel chemistry to Meyer's system in the first step. The formation of the ketone, 1-cyclohexene-1-one would appear to utilize the stronger RuO(hedta) oxidant in a reaction which probably parallels the oxidation of other secondary alcohols as described above (reaction (8)).

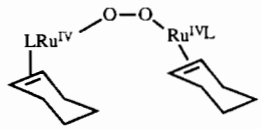
Other oxidants were used to test the generality of epoxidations of *cis*-stilbene with Ru(hedta) as catalyst. Hydrogen peroxide, H_2O_2 30% solution and OXONE, (HSO_5^-), were also used as the intended oxidants for *cis*-stilbene with Ru(hedta) as the catalyst. There was no *cis*-stilbene oxide formed with either H_2O_2 or OXONE. But for OXONE, $Ru^{III}L$ (L=hedta or *N,N'*-dimethyledda) still catalyzed oxidation of *sec*-phenethyl alcohol to acetophenone; see eqn. (9).



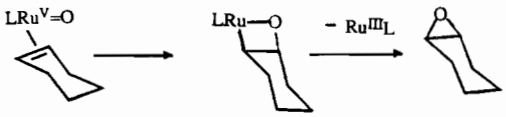
(9)

The results in this study again suggest that the source of oxygen transferred in the formation of *cis*-stilbene oxide is a metal–oxo species (and not a peroxo complex). The oxygen in this intermediate is derived from the oxidant employed for Ru^{III}(hedta) activation. In contrast, both t-BuOOH and HSO_5^- generate species which are sufficiently oxidizing of alcohols to promote H atom or hydride transfer oxidation of these substrates. This oxidation could occur without prior O–O cleavage in the Ru(hedta) $(OOSO_3H)^-$ intermediate and shows a differentiation between the activated catalytic species when t-BuOOH and HSO_5^- activate Ru^{III}(hedta).

The difference between our results for the hydroxylation of cyclohexene compared to epoxidation which was reported by Taqui Khan *et al.* [3] now requires an explanation. These workers noted that the kinetic analysis requires $Ru^{III}(edta)(H_2O)^-$ to associate with cyclohexene prior to an autooxidation step forming a μ-peroxo complex:



The rate determining step was described as the break up of this complex by O–O cleavage into a complex



which reacts rapidly, forming the epoxide [3, 4]. This process would require a *cis* orientation, and presumably a metallocyclic intermediate [4, 5] which reacts rapidly, forming the epoxide. In our present study we have formed the '$LRu^V{=}O$' entity directly which by-passes the prior association step indicated in the scheme

proposed by Taqui Khan *et al.* Thus the '$Ru^{V}=O$' species has the $LRu^{IV}-O^{-}\cdot$ character which can engage in H-atom abstraction from free cyclohexene. The hydroxyl rebound path would yield 2-cyclohexene-1-ol from authentic $LRu^{V}=O$. Therefore, the seeming difference between the reactivities of $LRu^{V}=O$ species toward cyclohexene would appear to be controlled by the relative order of olefin versus O-atom addition to the Ru^{III} center of polyaminopolycarboxylate complexes.

Acknowledgement

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