

Competitive catalytic epoxidation and oxidative cleavage of stilbene by ruthenium complexes

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Abstract

The catalytic oxidation of stilbenes, *cis*- and *trans*-, by iodobenzene in the presence of the diphosphino-complexes of ruthenium(II) [RuCl(LL)₂]PF₆ (LL = 1,3-bis(diphenylphosphino) propane, DPP; 1-diphenylphosphino-2-(2' pyridyl)ethane, PPY) gives rise to stilbene epoxides, *cis*- and *trans*-, and to benzaldehyde with distinctly different kinetic pathways. The reaction is first-order to the catalyst for the epoxidation and second-order for the oxidative cleavage, whereas the rate dependence upon substrate concentration indicates reversible formation of a common catalyst–substrate intermediate. © 1997 Elsevier Science B.V.

Keywords: Epoxidation; Oxidative cleavage; Stilbene; Ruthenium

1. Introduction

Ruthenium complexes are good epoxidation catalysts, by being high-valent oxo-ruthenium species as active intermediates in the oxygen transfer reactions. The mechanism of the reaction, however, is still not fully understood and also the detailed nature of the oxidizing species is not definitely established, since several types of oxo-ruthenium species can be formed with oxidation number ranging from IV to VIII. Most of the reported ruthenium-catalyzed epoxidations are indeed affected by important by-reactions generally leading to less valuable oxygenated compounds arising from the oxidative

cleavage of the double bond or, when β -hydrogens are available, products of the allylic oxidation. It appears essential to control the epoxidation process relatively to the non-epoxide reactions, which must be avoided or at least minimized: as an example, whereas 'naked' high valent oxoruthenium species, i.e., in the absence of organic ligands, only effect the oxidative cleavage of the olefins [1], ruthenium complexes are generally also able to promote epoxidation, although with various selectivities [2–19]. A better understanding of the factors influencing epoxidation would thus provide a basis for optimization of the catalytic oxidation of alkenes by ruthenium derivatives.

A recent critical review by Sheldon [2] on mechanistic and synthetic aspects of ruthenium-catalyzed epoxidations prompted us

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to re-examine a previously reported [4–6] alkene oxidation catalyzed by the five-coordinate phosphino-complexes $[\text{Ru}^{\text{II}}\text{Cl}(\text{LL})_2]\text{PF}_6$ ($\text{LL} = 1,3$ -bis(diphenylphosphino)propane, DPP, or 1-diphenylphosphino-2-(2'-pyridyl)ethane, PPY), with the aim to further elucidate the mechanistic features of the competitive epoxidation versus oxidative cleavage reaction. In this paper we selected stilbenes (*cis*- and *trans*-) as a model for alkene oxidation, because they give stilbene epoxides and benzaldehyde as the only products in balanced yields. In the previous papers we reported that in the presence of catalytic amounts of the above ruthenium-complexes, the reaction between iodosobenzene and a number of olefins yields the corresponding epoxides and varying amounts of by-products, mainly from the allylic oxidation and/or the oxidative cleavage of the double bond. Several lines of evidence supported that, upon reaction of the ruthenium(II) complexes under examination with PhIO, $\text{Ru}^{\text{IV}}=\text{O}$ groupings are formed, rather than $\text{O}=\text{Ru}^{\text{VI}}=\text{O}$, which is another common feature in ruthenium(II) chemistry: indeed, from the reaction mixtures paramagnetic oxo-bridged $[(\text{LL})_2\text{ClRu}^{\text{III}}(\text{O})\text{Ru}^{\text{III}}\text{Cl}(\text{LL})_2]^{2+}$ complexes were isolated, whose formation is more likely to take place upon reaction of the coordinatively unsaturated $[\text{Ru}^{\text{II}}\text{Cl}(\text{LL})_2]^+$ species and the putative mono-oxo $[\text{Ru}^{\text{IV}}\text{Cl}(\text{O})(\text{LL})_2]^+$ derivatives formed in situ [4].

2. Experimental section

2.1. Materials

Unless otherwise stated, all chemicals were purchased from Aldrich, stored at -20°C and used without further purification. Iodosobenzene (K and K Rare and Fine Chemicals) was stored at -20°C in the dark. The complexes $[\text{RuCl}(\text{DPP})_2]\text{PF}_6$ [20] and $[\text{RuCl}(\text{PPY})_2]\text{PF}_6$ [21] were prepared as previously described and stored at -20°C under argon.

2.2. Kinetic measurements

1 ml of a dichloromethane solution containing $0.01 \div 0.4$ mmol of the substrate, $0.002 \div 0.01$ mmol of the metal complexes and a gas-chromatographic standard (*n*-decane, 0.005 mmol) were stirred magnetically in a vial together with $11 \div 110$ mg of solid PhIO ($0.05 \div 0.5$ mmol) at 22°C . Organic analyses were performed on aliquots of the reaction mixture withdrawn at appropriate time with a hypodermic microsyringe, with a DANI 3800 gas chromatograph equipped with FID, using 30 m SE-30 capillary column (0.25 mm i.d.). The identity of each product was confirmed by comparison of the fragmentation pattern in the mass spectra obtained with a VG 16F mass spectrometer operating in the electron ionization mode at 70 eV. Reaction rates were determined at 22°C for early stages of the reaction and were reproducible to within 15%.

3. Results

The reactions between iodosobenzene and *cis*-stilbene in the presence of small amounts of the ruthenium(II) complexes give *cis*- and *trans*-stilbene epoxide and benzaldehyde, as the only identified oxidation products. The reaction with dilute *cis*-stilbene, 25 mM, and $[\text{Ru}^{\text{II}}\text{Cl}(\text{DPP})_2]\text{PF}_6$ catalyst, 2 mM, was investigated in details, to allow the identification by glc-ms of all organic compounds present in the reaction mixtures at various times (Fig. 1). All oxidation products were formed contemporarily since the very onset of the reaction and maintained their molar ratio throughout the reaction: direct control experiments confirmed that in the reaction conditions and within the times taken into consideration stilbene epoxides are not affected by rearrangement to benzaldehyde or by overoxidation, typically to benzophenone [17] and that no isomerization of *cis*-stilbene epoxide to the *trans*-isomer occurs. The presence of added benzaldehyde does not affect the forma-

tion of the epoxides, thus ruling out the possibility that epoxidation could be triggered via the well-known mechanism of aldehyde co-oxidation of alkenes [13]. The ratio between *cis*- and *trans*-stilbene epoxide remains essentially the same during the reaction (ca. 0.7) and does not apparently depend upon the initial concentration of the substrate. Quite unexpectedly, *trans*-stilbene was found in the reaction mixtures at the very beginning of the reaction in rather large amounts (ca. 25% of total alkene): the amount of *trans*-stilbene rapidly decreases to zero, paralleling the decrease of *cis*-stilbene, well before the end of the oxidation, without affecting the rate of formation of *trans*-stilbene epoxide. Since the substrate *cis*-stilbene used was 99% purity grade, extensive isomerization of *cis*-stilbene to *trans*-stilbene might occur in the presence of the catalytic system (no isomerization was indeed observed in the presence of the catalyst, but in the absence of the oxidizing agent). Mass balance, as calculated from the amount of benzaldehyde (divided per two), *cis*- and *trans*-stilbene epoxide and *cis*- and *trans*-stilbene, is close to 100% throughout the reaction: control experiments confirmed that benzal-

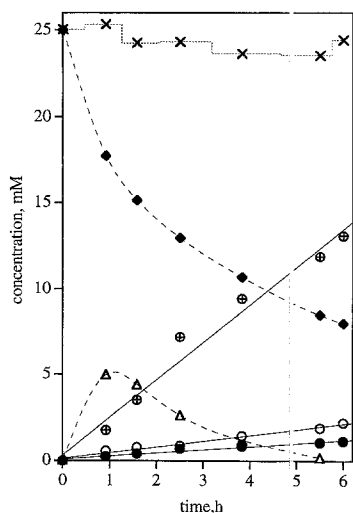


Fig. 1. Time course for the PhIO-oxidation of *cis*-stilbene, 25 mM, by $[\text{RuCl}(\text{DPP})_2]\text{PF}_6$, 2 mM, in CH_2Cl_2 ; 22°C: (●) *cis*-epoxide, (○) *trans*-epoxide, (◆) *cis*-stilbene, (Δ) *trans*-stilbene, (⊕) benzaldehyde ([PhCHO]:2), and (×) total mass balance.

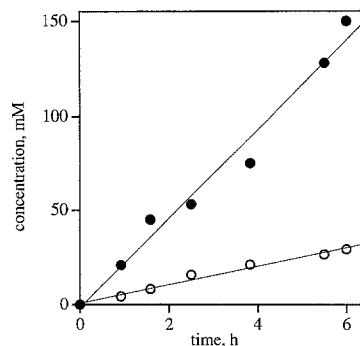


Fig. 2. Time course for the PhIO-oxidation of *cis*-stilbene, 25 mM, by $[\text{RuCl}(\text{DPP})_2]\text{PF}_6$, 2 mM, in CH_2Cl_2 ; 22°C: (●) iodobenzene, and (○) oxidation products, benzaldehyde + *cis*- and *trans*-stilbene oxide.

dehyde does not undergo further oxidation to benzoic acid.

Finally, the amount of iodobenzene released during the reaction, which is indicative of the amount of the oxidizing agent consumed, linearly increases, but in a ratio ca. 4:1 with the amount of oxygen transferred, as calculated from the amount of benzaldehyde and epoxides formed (Fig. 2). It should be noted that in the experiments at higher substrate concentrations the ratio between formed PhI and oxidation products is much closer to the expected value of 1:1, indicating that in the presence of excess substrate the so-called 'lost oxygen' reaction [14] becomes less important.

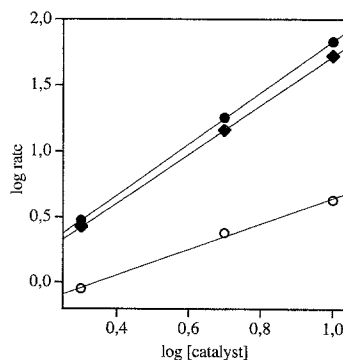


Fig. 3. Rate dependence upon $[\text{RuCl}(\text{DPP})_2]\text{PF}_6$ catalyst concentration for the PhIO-oxidation of stilbenes, 0.2 M, in CH_2Cl_2 ; 22°C: (○) oxidation of *cis*-stilbene to stilbene oxide, *cis*- and *trans*-, (●) oxidation of *cis*-stilbene to benzaldehyde, and (◆) oxidation of *trans*-stilbene to benzaldehyde.

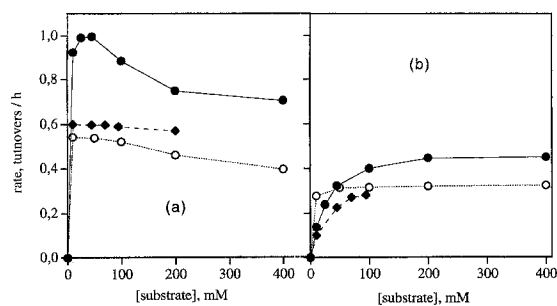


Fig. 4. Rate dependence upon substrate concentration for the PhIO-oxidation of stilbenes by $[\text{RuCl}(\text{LL})_2]\text{PF}_6$ (LL = DPP, PPY), 2 mM, in CH_2Cl_2 ; 22°C: (a) rate of benzaldehyde (PhCHO):2 formation; (b) rate of stilbene oxide formation (*cis*- and *trans*-). (●) *Cis*-stilbene and $[\text{RuCl}(\text{DPP})_2]\text{PF}_6$, (◆) *trans*-stilbene and $[\text{RuCl}(\text{DPP})_2]\text{PF}_6$, and (○) *cis*-stilbene and $[\text{RuCl}(\text{PPY})_2]\text{PF}_6$.

The kinetics of the epoxidation of *cis*- and *trans*-stilbene was examined in details in the previous paper [4], where a strictly linear rate dependence with respect to the catalyst concentration (Fig. 3) was reported, with reaction order to the substrate varying between zero and one (Fig. 4b). The competitive reaction of the oxidative cleavage of the double bond of the same substrates was investigated in the present work and was shown to obey a second order kinetic law to the metal catalyst (Fig. 3), with a peculiar rate dependence upon the substrate concentration, in which the rate increases with the concentration of the substrate until a maximum and then monotonically decreases, which is most

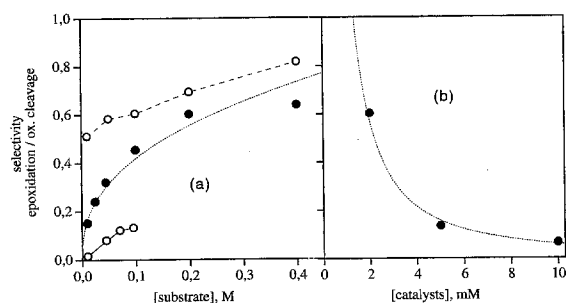
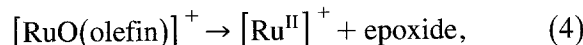
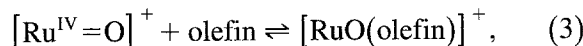
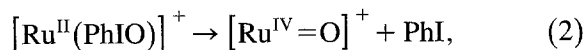
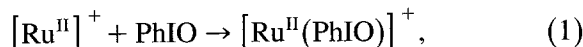


Fig. 5. Ratio of oxidative cleavage over epoxidation rates for the PhIO-oxidation of stilbenes by $[\text{RuCl}(\text{LL})_2]\text{PF}_6$ (LL = DPP or PPY), 2 mM, in CH_2Cl_2 ; 22°C: (a) dependence upon substrate concentration: (●) LL = DPP and *cis*-stilbene, (○) LL = DPP and *trans*-stilbene, and (◆) LL = PPY and *cis*-stilbene. (b) dependence upon $[\text{RuCl}(\text{DPP})_2]\text{PF}_6$ catalyst concentration: LL = DPP and *cis*-stilbene, ●.

clearly shown by the trend exhibited by the oxidative cleavage of *cis*-stilbene with the $[\text{Ru}^{\text{II}}\text{Cl}(\text{DPP})_2]\text{PF}_6$ catalyst (Fig. 4a). The extent of the oxidative cleavage reaction over the epoxidation is strongly dependent both upon the concentration of the substrate, with significant discrimination between the two examined catalysts, by being the *cis*-configuration better retained by the $[\text{RuCl}(\text{PPY})_2]\text{PF}_6$ complex (Fig. 5a), and, more markedly, upon the concentration of the catalyst, as expected by the fact that different reaction orders in the catalyst are exhibited by the two competitive reactions (Fig. 5b).

4. Discussion

The results indicate that the two oxidation reactions, i.e., epoxidation and oxidative cleavage, although competitive and based on the same catalytic system, proceed by different mechanisms. A simple mechanism was proposed for the epoxidation [4], which involves the fast formation of a ruthenium(IV) mono-oxo species upon reaction of PhIO with the starting complexes (Eqs. (1) and (2)) and the fast reversible formation of a stable reaction intermediate containing the metal complexes 'bonded' to both the oxygen to be transferred and the olefin (Eq. (3)), followed by a first-order slow step leading to the epoxides (Eq. (4)).



$$r_{\text{epox}} = V_{\text{max}}[\text{S}] / (K_{\text{m}} + [\text{S}]). \quad (5)$$

We found that each olefin epoxidizes at different rates, a strong indication for a reaction intermediate involving the olefin, which clearly rules out a rate determining step consisting in the formation of the oxidizing metal-species, as

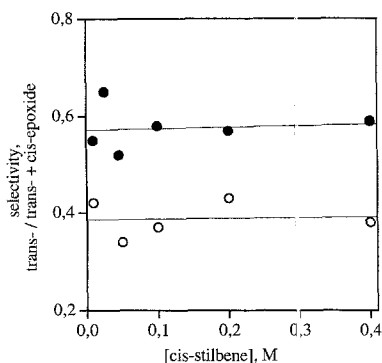
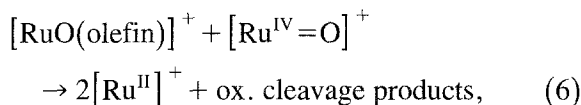


Fig. 6. Ratio of *trans*- to *cis*-stilbene epoxide formation rates vs substrate concentration for the PhIO-epoxidation of *cis*-stilbene by $[\text{RuCl}(\text{LL})_2]\text{PF}_6$, 2 mM, in CH_2Cl_2 ; 22°C: (○) LL = DPP, and (●) LL = PPY.

in the case, for example, of the epoxidations by Mn-porphyrins, where the oxo-species $\text{Mn}=\text{O}$ is slowly formed from a $\text{Mn}-\text{OCl}$ adduct [22]. Metal-iodosobenzene adducts, which are the likely precursors to the high-valent metal oxo complexes (Eq. (1)), have been also suggested as themselves competent as oxidizing reagent, that can react directly with olefins [14]. We were not able to distinguish between the two possibilities by kinetic data alone and, although no evidence for such adducts was obtained during the present investigation, we cannot rule out that the actual putative oxidizing species may be a $[(\text{LL})_2\text{CIRu}^{\text{II}}(\text{PhIO})]^+$ species, instead of the proposed $[(\text{LL})_2\text{CIRu}^{\text{IV}}=\text{O}]^+$ one: it should be noted however that this will only marginally affect the discussion of the kinetic data. Finally, the fact that the ratios of *cis*- to *trans*-stilbene oxide, formed upon epoxidation of *cis*-stilbene, are substantially independent upon the concentration of the substrate (Fig. 6), strongly suggests that isomerization depends upon a saturation mechanism. By treating the kinetic data of the epoxidation by the conventional Michaelis-Menten analysis (Eq. (5)), the values of K_m and V_{max} for each olefin were obtained by the Lineweaver-Burk method, where K_m can be regarded, as usual, as the equilibrium constant for the dissociation of the reaction intermediate into the catalyst and the substrate (Eq. (3)) and

V_{max} as the rate of the limiting step leading to the products in saturation conditions (Eq. (4)).

The distinctive experimental rate law found for the competitive reaction of oxidative cleavage, i.e., the second order in the catalyst, and the peculiar rate dependence on the substrate (Fig. 4a), is consistent with a mechanism involving again the pre-equilibrium described in Eq. (3), but followed by slow step, tentatively described in Eq. (6). The kinetic parameters are estimated assuming the kinetic law of Eq. (7).



$$r_{\text{ox. cleav.}} = K_m V'_{\text{max}} [\text{S}] / (K_m + [\text{S}])^2. \quad (7)$$

Eq. (7) only in part fits with the observed rate dependence: at higher concentration of the substrates an additional term, probably dependent upon the concentration of the substrate, becomes apparently important, likely arising from an independent oxidative cleavage of the double bond, which has been not further investigated. On this basis, the kinetic parameters for the oxidative cleavage can be estimated by the rate vs. [substrate] plot, by being the position of the maximum of Fig. 4a related to the value of K_m of pre-equilibrium 3 and the corresponding val-

Table 1
Kinetic parameters for the oxidation of stilbene (*cis*- and *trans*-) catalyzed by $[\text{RuCl}(\text{LL})_2]\text{PF}_6$ complexes^a

Catalyst (LL =)	Substrate	Epoxidation ^b		Oxidative cleavage ^c	
		K_m ^d	V_{max} ^e	K_m ^d	V'_{max} ^e
DPP	<i>cis</i>	30	0.54	35 ± 10	ca. 4.0
DPP	<i>trans</i>	30	0.33	30 ± 20	≤ 2.4
PPY	<i>cis</i>	20	0.31	30 ± 20	≤ 2.2

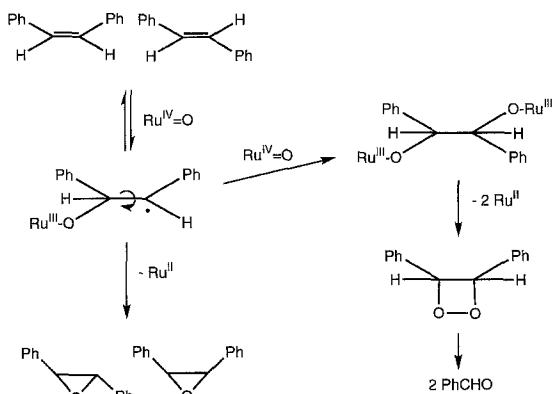
^a Catalyst, $[\text{RuCl}(\text{LL})_2]\text{PF}_6$ (LL = DPP, PPY), 2 mM, and substrate, 10–400 mM, in CH_2Cl_2 with solid PhIO; 22°C.

^b Rates for the epoxidation were determined by the amount of stilbene epoxides (*cis* and *trans*) formed; kinetic parameters were calculated by a Lineweaver-Burk analysis of the data (see Ref. [4]).

^c Rates for the oxidative cleavage were determined by the rates of formation of benzaldehyde divided per two; kinetic parameters were estimated from rate versus [substrate] plots (see text).

^d mM.

^e Turnovers/h.



Scheme 1. Proposed catalytic cycle for the PhIO-oxidation of stilbenes by $[\text{RuCl}(\text{LL})_2]\text{PF}_6$ complexes.

ues of the rate, rate_{max} , to the value of V'_{max} of reaction 6 ($V'_{\text{max}} = 4 \times \text{rate}_{\text{max}}$, according to Eq. (7)). The estimated values of K_m for the oxidative cleavage reactions agree considerably well with those calculated from the conventional Michaelis–Menten treatment of the competitive epoxidation reaction (Table 1), by being an indirect, although suggestive, indication that the two competitive reactions share the same pre-equilibrium (Scheme 1).

5. Conclusion

The kinetic behavior of the catalytic oxygenations under examination is remarkably similar to that of natural enzymes and of some synthetic manganese-porphyrins in related oxygenations of olefins [15,23,24]. For the case under examination all oxygenation products arise from a common reaction intermediate, which evolves via kinetically differentiated paths. The mechanistic conclusion drawn from our data has some relevance, since the mechanism of the oxidative cleavage is generally believed, but not fully proven, to involve a $[3 + 2]$ cycloaddition of a *cis*-dioxo moiety to the double bond [25]: however, very few *cis*- and *trans*-ruthenium-dioxo isomers sharing the same ligands have been compared and experimental data indicates that in many cases both *trans*-

and *cis*-dioxo complexes equally afford epoxides during the oxidation of alkenes [2,16,18,19], whereas very rarely mono-oxo- or *trans*-dioxo-ruthenium exhibits 100% selectivity in epoxidation.

The distinctly different [substrate]-rate dependencies of the epoxidation and of the oxidative cleavage found in the system under investigation make it possible, at least in principle, to divert the oxidation towards either the oxidative cleavage or the epoxidation, by simply changing the concentration conditions. At high substrate concentrations, where the experimental rates of the epoxidation reach a maximum and those of the oxidative cleavage approach zero, epoxides are expected to become the major products (see Fig. 5a). Since also the [catalyst]-rate dependencies are different for the two competitive reactions (first- versus second-order), major amounts of epoxides are expected to be obtained in the presence of diluted solutions of the catalyst, as clearly evidenced by the experimental trend depicted in Fig. 5b. The proven possibility to trigger significant changes in the chemoselectivity of the oxidation by varying the concentration conditions is noteworthy, for it suggests that one may ultimately generate 100% selectivity in the alkene epoxidation by an accurate mise a point of the reaction conditions. Finally, also an appropriate choice of the ligands around ruthenium(II) may lead to more favorable epoxide/benzaldehyde ratios: we observed that with the $[\text{RuCl}(\text{PPY})_2]^+$ catalyst, epoxidation of *cis*-stilbene becomes more important than in the case of the closely related $[\text{RuCl}(\text{DPP})_2]^+$ catalyst (Fig. 5a).

Acknowledgements

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