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Alkene Epoxidation by Ruthenium(II) Phosphine Complexes. A Kinetic Investigation

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Coordinatively unsaturated complexes of ruthenium(II) of the type $[RuCl(LL)_2]^+$, where LL is 1,3-bis(diphenylphosphino)propane or 1-(diphenylphosphino)-2-(2-pyridyl)ethane, effectively promote the epoxidation of olefins in the presence of iodosylbenzene and in low-coordinating media. Competition from oxidative cleavage and/or allylic oxidation is observed with some olefin. The kinetics of the epoxidation of 1-octene, *trans*-2-octene, cyclooctene, norbornene, styrene, *trans*-β-methylstyrene, and *cis*- and *trans*-stilbene have been investigated gas chromatographically, and the following conclusions are drawn. (i) The reaction order in the catalyst is 1; (ii) the reaction order in the olefins varies between 0 and 1; (iii) rates are different from each olefin examined. It is suggested that the rate-determining step consists in the breakdown of an oxo–metal intermediate containing the olefin. K_M and V_{max} values are calculated from the Michaelis–Menten equation, indicating that the relative reactivity of olefins toward catalytic epoxidation falls into a relatively narrow range. Competition experiments have been performed that confirm the K_M data obtained by the Lineweaver–Burk analyses. Stereospecific epoxidation is achieved with *trans*-olefins (stilbene, 2-hexene, and 2-octene), whereas the corresponding *cis*-olefins produce high yields of *trans*-epoxides, pointing to a substantially radicaloid character of the reaction intermediate.

Introduction

The catalytic functionalization of various types of hydrocarbons with terminal oxidants, such as non-metal oxides, is of both chemical and biochemical importance. Among such transformations, the metal-catalyzed conversion of olefins to their epoxides poses an intriguing synthetic as well as theoretical challenge. Metalloporphyrins have been studied extensively,[1] owing to their direct relationship to enzymatic oxidations, but the same catalytic epoxidations are mimicked by metal complexes of other macrocycles and even of more simple ligands.[2] Although in general the utility of these catalytic systems for effective epoxidation is so far very limited, they are useful for mechanistic studies to demonstrate the role of the oxometal intermediate in the oxidation process.

Among the well-established oxidizing oxo reagents for the functionalization of olefins are ruthenium and osmium oxides and, in general, catalyst–oxidant systems involving a ruthenium salt, usually $RuCl_3$, and a terminal oxidant, like hypochlorite or periodate. Ruthenium-based catalysts typically promote the oxidative cleavage of double bonds to ketones (or aldehydes and/or carboxylic acids).[3] Epoxidations have also been reported to occur with a periodate/$RuCl_3$ system in the presence of bipyridyl or substituted phenanthrolines,[4] and closely related behaviors have been observed for high-valent oxo derivatives of ruthenium containing polydentate nitrogen donors and using hypochlorite as oxidant.[5,6]

We recently reported that simple phosphino complexes of ruthenium(II) and osmium(II) of composition $[MCl(LL)_2]^+$ (LL = 1,3-bis(diphenylphosphino)propane, DPP, and 1-(diphenylphospino)-2-(2-pyridyl)ethane, PPY) could also mediate the transfer of oxygen atoms from iodosylbenzene and other single-oxygen oxidants to olefins.[7] In this study we wish to followup on this preliminary report, our principal focus being now to demonstrate how the putative oxo–metal species enters the catalytic cycle and to delineate the mechanism of oxygen atom transfer from the oxo–metal species to the olefin substrates.

Mechanistic and kinetic studies reveal that these catalyzed reactions are first order in [M] and zero order in the substrate at higher, but still moderate, alkene concentrations, indicating that a prior coordination of olefin might be an important step. Epoxidation rates satisfactorily follow Michaelis–Menten trends for a number of substrates, apparently with the decomposition of an oxo–metal/olefin adduct to epoxide (and the metal complex) being the rate-determining step of the catalytic cycle. The relationship, in terms of kinetic behaviors, of these catalysts to the biomimetically relevant manganese porphyrins recently examined by Collman and Meunier[8] is an important consideration.

Experimental Section

Materials. Olefins (commercial samples) were purified by chromatography on alumina and stored at −20 °C. Iodosylbenzene was a commercial product from K&K Labs. 1-(Diphenylphosphino)-2-(2-pyridyl)ethane (PPY) was prepared from diphenylphosphine and 2-vinylpyridine.[9] 1,3-Bis(diphenylphospino)propane (DPP) was purchased from Strem Chemicals. The epoxides used for gas chromatographic standardization were commercial products or, alternatively, prepared by treatment of the olefins with *m*-chloroperbenzoic acid.[10] The complexes $[RuCl(LL)_2]Y$ (LL = DPP, PPY; Y = ClO_4, PF_6) were prepared, as previously published,[11] by refluxing ethanolic suspensions of the corresponding *trans*-$[RuCl_2(LL)_2]$ complexes, in the presence of excess $NaClO_4$ or NH_4PF_6.

$[Cl(PPY)_2RuORu(PPY)_2Cl](PF_6)_2$. A 430-mg sample of $[RuCl(PPY)_2]PF_6$ (0.5 mmol) dissolved in 20 mL of CH_2Cl_2 was stirred in the presence of PhIO (1.1 g, 5 mmol), until the solution turns green. By addition of ethanol, a green product precipitates (yield 50%). Anal. Calcd for $C_{76}H_{72}Cl_2F_{12}N_2OP_6Ru_2$: C, 52.36; H, 4.16; N, 3.21; Cl, 4.07. Found: C, 50.8; H, 4.1; N, 3.0; Cl, 3.9. Conductivity data from the plot of Λ_e vs. the square root of the equivalent concentration, according to the Onsager equation $\Lambda_e = \Lambda_0 + AN^{1/2}$, are $\Lambda_0 = 97$ cm^2 Ω^{-1} equiv^{-1} and $A = 490$ cm^2 Ω^{-1} equiv^{-1} N$^{-1/2}$ (0.3–5 mM in CH_3NO_2, 20 °C). I_{max} (900–300 nm in CH_2Cl_2) is at 635 nm. μ_{eff} (per metal atom, Gouy's method) = 1.7 μ_B at 20 °C.

Instrumentation. UVV and IR spectra were recorded on Perkin-Elmer Lambda 5 and 781 spectrometers, respectively. NMR spectra were recorded on a JEOL FX 90Q FT spectrometer. Organic analyses were made on a DANI 3800 gas chromatograph equipped with FID, using a 2-m Ucon LB 550 on Chromosorb W-AW 60–80-mesh packed column

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Table I. Ruthenium-Catalyzed Epoxidation of Alkenes[a]

	% conversn (% epoxide)[b]			
alkene	$[RuCl(DPP)_2]^+$		$[RuCl(PPY)_2]^+$	
norbornene	7	(60)	13	(45)
cyclooctene	4	(65)	7	(55)
styrene	7	(35)	12	(35)
trans-β-methylstyrene	21	(25)[c]	32	(45)[c]
cis-β-methylstyrene	20	(20)[d]	27	(25)[d]
trans-stilbene	16	(20)[c]	15	(25)[c]
cis-stilbene	20	(35)[d]	17	(40)[d]
trans-2-octene	6	(40)[c]	6	(40)[c]
cis-2-octene	7	(35)[d]	*e*	
1-octene	1	(65)	1	(85)

[a] Alkene, 0.1 M, and $[RuCl(LL)_2]ClO_4$, 2 mM, treated with PhIO (molar ratio with catalyst = 100:1), in dichloromethane, at 22 °C. [b] Calculated on the amount of olefin converted into various oxidation products, after 10 h (selectivity in epoxide). [c] Only *trans*-epoxide. [d] *cis*- and *trans*-epoxide. [e] Not determined.

(2 mm i.d.) or a 30-m SE-30 capillary column (0.25 mm i.d.). The identify of each product was confirmed by comparison of the mass spectral cracking pattern from a VG 16F mass spectrometer operating in the electron ionization mode at 70 eV.

Procedure for the Catalytic Oxidations. A 15-mg (68-mmol) sample of iodosobenzene was suspended in 1 mL of a dichloromethane solution containing 0.05–2.1 mmol of olefin, 2 μmol of metal complexes, and a gas chromatographic standard (*n*-decane, 5 mM). The suspension was stirred magnetically in a 2-mL minivial at 22 °C and GLC analyses were performed on aliquots withdrawn periodically by a hypodermic microsyringe. Previously filtered and unfiltered samples gave the same results. The reactions were carried out both under nitrogen and in the air, as the epoxide formation was not affected by the presence of air. Reaction rates were determined at early reaction times (up to 10 cycles) and were reproducible to within 10–15%.

Determination of K_M and V_{max}. K_M and V_{max} for the epoxidations were obtained from the Lineweaver–Burk analyses[12] of rate^{-1} vs [substrate]$^{-1}$ plots. Initial rates were measured at four (or more) olefin concentrations, ranging from 0.5 to 10 times the K_M value for each substrate, at 2 mM catalyst concentration. In the case of styrene, four different concentrations of $[RuCl(DPP)_2]ClO_4$ were examined (0.45–25 mM), in order to determine the reaction order in the catalyst. Estimate (most probable) errors on the reported values range between 10–15% for V_{max} and 20–25% for K_M.

Results and Discussion

The olefin consumed during the oxidation was determined as the difference between the amount charged and that recovered. On this basis, many olefins are converted selectively to the corresponding epoxides, with cyclohexene and, to some extent, phenyl-substituted olefins being the outstanding exceptions. Conversions, reported in Table I, are indicative of the catalytic efficiency of the oxygen transfer reaction. However, the catalytic activity of the complexes, based on the conversion of the terminal oxidant, is higher. Thus, since the formation of iodobenzene from iodosylbenzene also proceeds competitively in the absence of an olefin substrate, the listed yields only reflect the relative reactivity of the olefins.

When a mixture of 2 μmol of $[RuCl(DPP)_2]ClO_4$ and 0.2 mmol of iodosylbenzene was allowed to react with a solution of norbornene (0.1 mmol) in dichloromethane (1 mL), a slow reaction (less than 0.4 turnover/h) ensued to produce norbornene oxide in a 60% yield. In addition, minor amounts of byproducts were found, among which was cyclopentane-1,3-bis(carboxaldehyde). Cyclooctene oxide was formed in a 65% yield, when cyclooctene was treated under the same conditions, together with products of ketonization, such as cyclooctanone and cyclooctane-1,2-dione. At the contrary, cyclohexene was converted mainly into products of allylic attack (cyclohexen-3-ol, cyclohexen-3-one, etc.), affording only traces of cyclohexene oxide.

Olefins bearing aromatic substituents lack the selectivity observed in the norbornene and cyclooctene systems. Styrene oxide was produced in a 35% yield from styrene, whereas benzaldehyde was the major detectable product. Since blank experiments showed that styrene oxide was stable toward further oxidation under the same reaction conditions, it is concluded that benzaldehyde is likely to be produced from an independent oxidative cleavage pathway. Stilbenes and β-methylstyrenes (cis and trans) were more rapidly converted (up to ca. 1 turnover/h), but again benzaldehyde was the dominant detectable oxidation product.

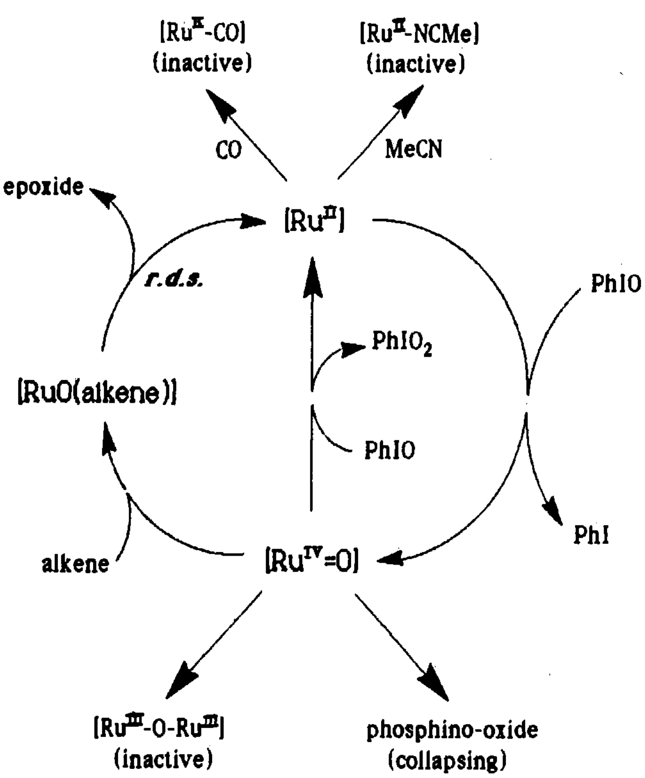
Linear alkenes, like 1- and 2-hexenes and 1- and 2-octenes, were selectively, but very slowly (less than 0.1 turnover/h), oxidized into the corresponding epoxides. The other five-coordinate ruthenium(II) complex examined, i.e. $[RuCl(PPY)_2]ClO_4$, gave quite similar results, in terms of both activity and selectivity. Coordinating solvents, like acetonitrile, completely poison the catalytic system, with formation of inactive, coordinatively saturated $[RuCl(CH_3CN)(LL)_2]^+$ adducts.

The active species responsible for the oxygen atom transfer to the olefins is thought to be a ruthenium(IV)–oxo complex, formed by reaction of PhIO with the ruthenium(II) derivatives by a process similar to that established for a number of other metal complexes. Such a reactive species is capable of isotopic exchange with [^{18}O]water, thus accounting for the efficient incorporation of labeled oxygen into norbornene epoxide (30%) during the catalytic oxidation of norbornene in the presence of labeled water.[7] Indeed, the isotopic incorporation represents the best evidence for an independent oxo complex, since an alternative pathway via a prior exchange with the terminal oxidant must be ruled out (the unreacted PhIO upon recovery contained no isotopic label, and exchange of the epoxide with water is ruled out).

This metal–oxo derivative might be reactive, as expected for a species able to epoxidize alkenes and hydroxylate unactivated alkanes.[13] We propose that the next step involves the reaction of this intermediate not only with the organic substrates, to give the desired reactions, but also with iodosobenzene (to give iodoxybenzene), with the phosphinic ligand (to give diphosphine oxide) and with other metal species, including the starting complex, to give inactive products (Scheme I).

Disproportionation of PhIO to PhI and $PhIO_2$ is commonly catalyzed by a variety of metal catalysts,[14,15] including [RuCl-

Scheme I



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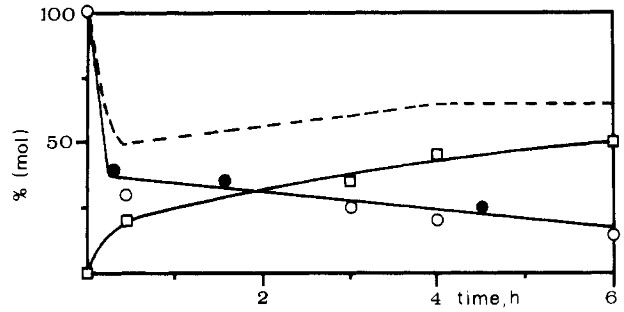

Figure 1. Composition of the reaction mixtures during the oxidation of 1 M norbornene with PhIO, catalyzed by 2 mM $[RuCl(DPP)_2]PF_6$ (CH_2Cl_2, 22 °C): intact $[RuCl(DPP)_2]PF_6$, measured by ^{31}P NMR (○) and by UVV (●); oxidized $[RuCl(DPP)_2]PF_6$, measured by ^{31}P NMR from the amount of diphosphine oxide formed (□), calculated as percentages of the starting catalyst. The dotted line represents the sum of the two quantities.

$(DPP)_2]PF_6$ and other ruthenium derivatives.[16] $PhIO_2$ was isolated at the end of the reaction and characterized by IR spectra, where two diagnostic strong bands are observed at 710 and 760 cm^{-1}, attributed to the I=O stretchings.[17]

The fate of the catalyst has been followed by monitoring the UVV and ^{31}P NMR spectra during the reaction. The $^{31}P\{^1H\}$ NMR spectrum of $[RuCl(DPP)_2]PF_6$ (two triplets centered at 45.7 and 2.95 ppm, J_{pp} = 30 Hz, due to the coordinated diphosphines, and a septet centered at −142 ppm, J_{PF} = 710 Hz, from PF_6^-) remains unchanged after the addition of excess norbornene, indicating no interaction between the olefin and the complex. By further addition of PhIO, oxidation of norbornene occurs, together with the formation of diphosphine oxide (singlet at 32.6 ppm). However, while the intensity of this peak is in a 2:3 ratio with the resonances due to the intact $[RuCl(DPP)_2]PF_6$, the combined integrals of all these signals are only in a 2:1 ratio compared with that of the septet from the PF_6^- anion. A barely detectable broad signal in the 50–80 ppm region accounts for about the 50% of the starting material and is assigned to a paramagnetic species, possibly the active intermediate. After 6 h of reaction, with the catalytic system still active, the situation is only slightly changed (Figure 1). The NMR data are fully consistent with the UVV spectra of the reaction mixtures, where the distinctive absorptions of $[RuCl(DPP)_2]PF_6$, at 550 and 445 nm, appear definitely less intense.

The reaction of $[RuCl(DPP)_2]PF_6$ with PhIO, in the absence of olefin, leads to the formation of green paramagnetic products with erratic elemental analyses and variable characteristics of solubility. Only in the case of $[RuCl(PPY)_2]PF_6$ was the most soluble fraction of the green product satisfactorily analyzed as $[Cl(PPY)_2Ru(\mu\text{-}O)Ru(PPY)_2Cl](PF_6)_2$. Magnetic moment per metal atom (1.7 μ_B) is close to that expected for a low-spin d^5 ion, whereas conductivity data at variable concentration indicate that the compound is 2:1 electrolyte (see Experimental Section). No absorption due to Ru=O stretching is observed in the 800-cm^{-1} region, whereas the ^{31}P NMR spectra only show the septet of the PF_6^- anion and broad signals in the 30–70 ppm region.

All the isolated green paramagnetic products, likely μ-oxo derivatives of Ru(III) of various molecular complexities, are catalytically inactive for both the oxidation of the olefins and the disproportionation of PhIO. The formation of these compounds, which are *not* the reaction intermediates, demonstrates the reactivity of the putative oxo derivative. Indeed, monooxo complexes of Ru(IV) are often reported to be unstable and to undergo either disproportionation to Ru(II) and Ru(VI)–dioxo species[18] or conversion into μ-oxo–Ru(III) derivatives.[19,20]

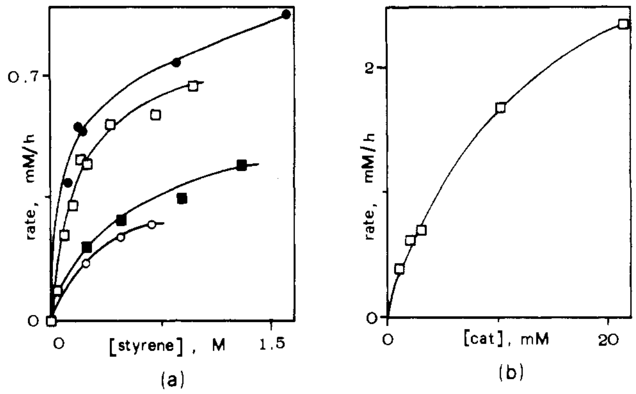

Figure 2. Epoxidation rate of styrene with PhIO, catalyzed by $[RuCl(DPP)_2]ClO_4$ (CH_2Cl_2, 22 °C): (a) effect of substrate concentration at 0.45 (○), 1 (■), 2 (□) and 3 (●) mM catalyst concentration; (b) effect of catalyst concentration (substrate, 1 M).

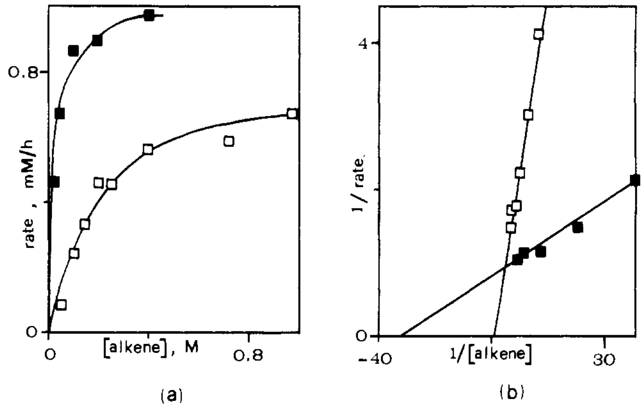

Figure 3. Epoxidation rate of styrene (□) and cis-stilbene (■) with PhIO, catalyzed by 2 mM $[RuCl(DPP)_2]ClO_4$ (CH_2Cl_2, 22 °C): (a) effect of substrate concentration, (b) reciprocal plots.

Table II. Kinetic Parameters for Epoxidation Catalyzed by Ruthenium Complexes[a]

	$[RuCl(DPP)_2]^+$		$[RuCl(PPY)_2]^+$	
alkene	K_M[b]	V_{max}[c]	K_M[b]	V_{max}[c]
styrene	0.22	0.41	0.08	0.28
cyclooctene	1.63	0.79	0.12	0.77
norbornene	0.49	0.76	0.12	0.58
trans-stilbene	0.03	0.33	*d*	*d*
cis-stilbene	0.03	0.54	0.02	0.31
trans-β-methylstyrene	0.16	0.78	<0.01	0.71
1-octene	0.20	0.03	*d*	*d*
trans-2-octene	0.30	0.15	0.04	0.18

[a] Alkene, 0.015–1.7 M, and $[RuCl(LL)_2]ClO_4$, 2 mM, treated with PhIO (molar ratio with catalyst = 100:1), in dichloromethane, at 22 °C. [b] Units: mol/L. [c] Units: turnover/h. [d] Not determined.

The rates of styrene epoxidation by PhIO were measured in dichloromethane in the presence of catalytic amounts of $[RuCl(DPP)_2]ClO_4$ (Figure 2). The reaction is substantially first order in the catalyst, the slightly negative effect at higher catalyst concentrations being attributable to a diversion of the active oxo–metal derivative, likely the formation of μ-oxo species, that might be dependent on the concentration of the catalyst.

Instead, the reaction order in the substrate varies, for styrene and other aliphatic and aromatic alkenes, between 1 and 0 (Figure 3), zero order being generally approached at moderate concentrations (down to 0.4 M). Therefore, this effect is hardly at-

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Table III. Ruthenium-Catalyzed Competitive Epoxidations[a]

	% epoxide		
alkene (+competitor)	found	calcd	
cis-stilbene, 0.3 M(+styrene, 0.6 M)	74	83[b]	57[c]
cyclooctene, 0.5 M(+*trans*-2-octene, 0.5 M)	57	49[b]	84[c]

[a] $[RuCl(DPP)_2]ClO_4$, 2 mM, treated with PhIO (molar ratio with catalyst = 100:1), in dichloromethane, at 22 °C; within 10 h of reaction. [b] Calculated by using eq 2 and kinetic parameters reported in Table II. [c] Calculated by using V_{max} values reported in Table II.

tributable to modifications in the characteristic of the medium, even if a change in mechanism that is dependent on the olefin concentration could be taken into consideration.

The kinetic data, which follow the Michaelis–Menten equation (1), suggest that the rate-determining step of the catalytic cycle

$$1/\mathrm{rate} = 1/V_{max} + K_M/V_{max}[\mathrm{substrate}] \qquad (1)$$

is the breakdown of a relatively stable intermediate, which must contain the olefin, because, at saturating levels, *each olefin is converted at a different rate* (Table II). Since there is no evidence for simple olefin adducts, an oxo–metal/olefin intermediate is a likely explanation of the kinetic behavior; on the other hand, we presented evidence for the existence in the reaction mixtures of large amounts of catalytically active species, other than the starting complexes. In this formulation the oxygen transfer would occur in two separable steps, namely the binding of the olefin to the oxo–metal species (measured by K_M) and the decomposition of such intermediate (measured as V_{max}).

Kinetic studies, where two different olefins are in competition (Table III), confirmed that, under steady-state conditions, the epoxidation rate of a reactive olefin, such as styrene, is inhibited by the presence of *cis*-stilbene, for which a much smaller value of K_M has been calculated (see Table II). Experimental ratios of the epoxidation rates for the two competing substrates, A and B, are satisfactorily related by eq 2 to the experimental V_{max} and K_M values listed in Table II.

$$V^A/V^B = [A]V_{max}{}^A K_M{}^B/[B]V_{max}{}^B K_M{}^A \qquad (2)$$

K_M and V_{max} (Table II) are not dramatically different from each other, despite the significant differences in the nature of the substituents, aromatic and aliphatic, at the double bond in the various olefins examined. On the contrary, the nature of the donor atoms set in the catalyst, while only slightly affecting V_{max}, has a marked effect on the K_M values, which are definitely smaller for all the examined substrates in the case of $[RuCl(PPY)_2]^+$ with respect to the $[RuCl(DPP)_2]^+$ catalyst. The enhanced stability of the reaction intermediate is reasonably attributable to the less stringent steric requirements of the PPY ligand.

Stereochemistry indicates predominant retention of configuration at the trigonal carbon center in the case of trans isomers of β-methylstyrene, stilbene and 2-octene, which by and large afford only *trans*-epoxides. Instead, *cis*-olefins undergo extensive loss of stereoselectivity upon epoxidation, with the *trans*- and not the *cis*-epoxides being the major products (Table IV). These results are reminiscent of driving forces for rearrangement of cisoid configurations in olefins and epoxides, which are greater than those of their transoid counterparts. However, since olefins are always recovered unrearranged and since *cis*- and *trans*-stilbene are here epoxidized at very similar rates, we interpret the poor retention of stereochemistry to auger a relatively long-lived intermediate, capable of isomerization by α,β-bond rotation. The appearance of isomerization in the epoxidation of *cis*-olefins points to the formation of radical or carbocationic intermediates, assuming that the rate of ring closure is lower than that of bond rotation.

The fact that no evidence of the formation of rearrangement products (such as phenylacetaldehyde in the case of the oxidation of styrene) have been observed further supports a radicallike character of the intermediates. It should be noted that this conclusion is somewhat in contrast with the poor discrimination, in terms of V_{max}, between the different olefins, where aromatic substituents to the double bond are reasonably expected to have a significant influence on the lability of a radicaloid intermediate.

Table IV. Stereochemistry of Epoxide Formation[a]

alkene	% *trans*-epoxide	% *cis*-epoxide
trans-stilbene	>99	<1
cis-stilbene	60	40
trans-β-methylstyrene	>99	<1
trans-2-octene	>99	<1
cis-2-octene	35	65

[a] Alkene, 0.1 M, and $[RuCl(DPP)_2]ClO_4$, 2 mM, treated with PhIO (molar ratio with catalyst = 100:1), in dichloromethane, at 22 °C; product ratios obtained within 10 h of reaction.

Conclusions

The catalysis of olefin epoxidation by the $[RuCl(LL)_2]^+$ complexes, although not particularly exciting in terms of activity and selectivity, if compared with similar metal-catalyzed systems based either on the same metal or on the same terminal oxidants offers an opportunity to investigate the intimate mechanism of the oxygen transfer reaction. Our kinetic results show in fact that the alkene binds to the metal–oxo species, forming a relatively stable intermediate, whose decomposition represents the rate-determining step of the process. It should be noted that very commonly,[14] but with the notable exception of the manganese–porphyrin systems described recently,[8] formation of an olefin adduct with the active oxo–metal species is either absent or unimportant: epoxidations of alkenes by $[Ru(O)(bpy)_2(py)]^{2+}$ or $[Ru(O)(bpy)_2(PR_3)]^{2+}$ are reported to be first order in the substrate.[5,21] *Significantly, in both cases, the monooxo species, unlike those of the closely related* $[RuCl(LL)_2]^+$ *complexes examined here, are sufficiently stable (inert?) to be isolated.*

We have provided some insight into the viability of the oxidative system based on the $[RuCl(LL)_2]^+$ cations, as follows. (a) It is capable of epoxidizing a variety of diverse olefins with good selectivity, with the epoxidation of 1-alkenes being especially notable (terminal alkenes are usually among the least reactive olefins and in metal-catalyzed epoxidations). (b) The limited conversions are not due to an inactive catalyst. Quite the contrary, oxygen transfer to olefins may occur in competition with other pathways, since the ruthenium(II) complexes are capable of readily utilizing the terminal oxidant. The deficit in the oxidation equivalents is attributable to effective competition from disproportionation of the oxidants, catalyzed by the metal itself. (c) The active species might be an oxo cation, which is capable, contrary to iodosylbenzene, of isotopic exchange with $[^{18}O]$water. A significant fraction of the metal complex is present in the reaction mixtures as a paramagnetic phosphinic species, likely the reaction intermediate. The catalysts are slowly destroyed via either a progressive oxidation of the ligands or formation of oxo-bridged species. (d) The relative reactivities of various olefins are encompassed in a narrow range. Thus only a factor of 25 separates the most reactive (norbornene) from the least reactive (1-octene) alkene (see Table II for V_{max} values). (e) Inspection of the K_M values reveals that alkenes bearing aromatic substituents bind somewhat more efficiently (lower K_M) than aliphatic or cyclic alkenes. Negligible geometric preferences are observed, *cis*-stilbene binding as well as the trans isomer. (f) The oxygen transfer to various *Z*-olefins occurs with poor stereochemical retention, pointing to an intermediate that is radicaloid in character.

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Registry No. PhIO, 536-80-1; $[RuCl(DPP)_2]^+ClO_4^-$, 14797-73-0; $[RuCl(PPY)_2]^+ClO_4^-$, 118589-14-3; $[Cl(PPY)_2RuORu(PPY)_2Cl](PF_6)_2$, 118725-06-7; $[RuCl(PPY)_2]PF_6$, 59560-68-8; norbornene, 498-66-8; cyclooctene, 931-88-4; styrene, 100-42-5; *trans*-β-methylstyrene, 873-66-5; *cis*-β-methylstyrene, 766-90-5; *trans*-stilbene, 103-30-0; *cis*-stilbene, 645-49-8; *trans*-2-octene, 13389-42-9; *cis*-2-octene, 7642-04-8; 1-octene, 111-66-0.

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